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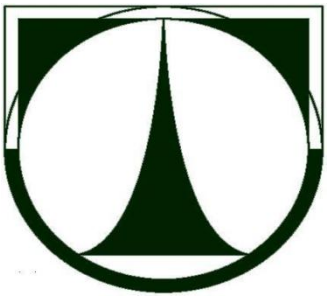

Ph.D. Thesis

2013 **ING. IBA GAYE**

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COMPARISON OF PROPERTIES OF ORGANIC AND CONVENTIONAL COTTON

STUDY PROGRAM: PhD Textile Engineering

STUDY: Textile Technics and Material Engineering

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Disclaimer:

I declare that my dissertation on comparing the properties of organic and conventional cotton, I developed independently under the leadership of the work and using information from professional literature and others information sources that are cited in the work and are also listed in the literature sources. As the author of the dissertation, I did not infringe the copyright of third parties, in particular I did not intervene illegally in foreign copyrights personality and I am fully aware of the consequences of the breach of § 11 and the following the Copyright Act 121/2000 Coll.

Abstract:

This work presents a comparison of the properties of conventional and organic cotton, using apparatus which are available at the Faculty of Textile and TUL, an analysis of cotton was made with the raster electron microscope SEM VEGA TS 5130, the physicochemical properties with GC / MS, analytical method of gas chromatography, the mechanical properties of both types of cotton were studied in Labor dynamometer test, strength was measured using Pressley Tester instrument response and fibers on the dynamic mechanical analyzer DMA., cotton maturity was determined using a polarizing microscope, using the apparatus Micronaire for fineness, staple length with staple diagram, thermal properties with the differential scanning calorimeter (DSC) and thermo gravimetric analyzer TGA. To detect the presence of pesticides in samples of cotton, gas chromatography with mass detector Saturn 2000 was employed and t5he results were compared to those obtained from the gas chromatography mass spectrum GC / MS. On the basis of these results it was concluded that the gas chromatographic method can be used to detect pesticides in cotton samples and can be applied to all natural fibers of plant origin. In this way, they can be distinguished as organic and conventional cotton, thus contributing to the certification of organic cotton and substances of vegetable origin. Analysis, which is introduced in this thesis, demonstrates difference in conventional and organic cotton from Senegal, Egypt, Russia and India.

Abstrakt:

Tato práce se zabývá porovnáním vlastností konvenční a organické bavlny pomocí přístrojů, které jsou k dispozici na fakultě textilní a na TUL, fyzikálně chemické vlastnosti jsou zjišťovány pomocí plynové chromatografie s hmotnostním spektrem varian 3800/2000, měřením extraktu organické a konvenční bavlny pomocí elektrochemických biosensorů acetylcholinesterazy. Byla provedena anályzu bavlny na rastrovacím elektronovém mikroskopu SEM VEGA TS 5130,analyzoval jsem také fyzikálně chemické vlastnosti pomoci GC/MS analytická metoda plynové chromatografie, některé mechanické vlastnosti obou druhů bavlny byly zkoumány na dynamometru Labor test, svazková pevnost byla měřena pomocí přístroje Pressley Tester a odezva vláken na dynamickém mechanickém analyzátoru DMA.zralost bavlny byla stanovena pomocí polarizačního mikroskopu, jemnost pomocí přístroje Micronaire, délka pomocí staplového diagramu, termické vlastnosti na diferenčním skenovacím kalorimetru (DSC) a na termogravimetrickém analyzátoru TGA. Pro zjištění přítomnosti pesticidů na daných vzorcích konvenční a organické bavlny byl použit přístroj pro plynovou chromatografii s hmotnostním detektorem Saturn 2000. Byly porovnány výsledky získané zplynové chromatografie hmotnostního spektra GC/MS a na základě těchto výsledků bylo konstatováno, že metodu plynové chromatografie lze použít k detekci pesticidů u bavlněných vzorků a lze je aplikovat pro všechna přírodní vlákna rostlinného původu. Tímto způsobem se mohou odlišovat organické a konvenční bavlny, a tím přispět k certifikování organických látek rostlinného původu. Analýzou, která je v práci uvedena byla prokázána odlišnost konvenční a organické bavlny ze Senegalu, Egypta, Ruska a Indie.

Contents:

List of symbols and abbreviations:

FAO	United Nations Food and Agriculture	
ISRA	Senegalese Institute for Agricultural Research	
CCIC	International Cotton Advisor Committee	
INP	National Institute of Pedagogy	
Enda	Environment and Development in the Third World	
KTM	Department of Textile Materials	
RI	The retention index	
PI	Index Pressley	
TGA	Thermo gravimetrical analysis	
SEM	Scanning Electron Microscope	
RM	Reference Material	
DMA	Dynamic mechanical analysis	
IU	Ion speed	[m / s]
GC	Gas chromatography	
MS	Mass spectrum	
Prob	Probability	
DSC	Differential scanning calorimetry	
F	Force	[N]
Fr	Relative strength	[c N tex^{-1}]
L	Length	[m]
ε	Absolute Extension	[%]
E	Modules	[G Pa]
P	Pressure	[Pa]
S	Cross-sectional area	[m^2]
Q	Heat	[J]
T	Time	[s]
T_m	Melting point	[° C]
T_g	Glass transition temperature	[° C]
V	Volume	[m^3]
A_{max}	Elongation to break	[%]

a-1	Egyptian cotton	
b-1	Russia cotton	
c-1	India cotton	
AH	Free enthalpy	[J/g]
FT-IR	Fourier transform infrared spectroscopy	

1. Introduction

Textile industry is a fast growing industry that requires huge amounts of water, energy, chemicals, and large amount of pesticides in order to protect cotton plant against insects and weeds attack. Cotton finishing processes use chemicals, which leads to high amounts of laundry waste water streams causing such problems and organic textile processing procedures are the environment friendly, economically better and can save water, time and chemicals. Cotton is the most important natural textile fiber, as well as cellulosic textile fiber in the world, used to produce apparel, home furnishings, and industrial products. World wide about 40% of the fiber consumed is cotton. Cotton is grown mostly for apparel application but it is also a food crop (cotton seed) the major end uses for cotton seeds are vegetable oil for human consumption; whole seed, meal, and hulls for animal. Cotton fibers are seed hairs from plants of the order Malvales, family Malvaceae, tribe Gossypieae, and genus Gossypium. Botanically, there are four principal domesticated species of cotton of commercial importance: hirsutum, barbadense, aboreum, and herbaceum. Thirty-three species are currently recognized; however, all but these four are wild shrubs of no commercial value. Each one of the commercially important species contains many different varieties developed through breeding programs to produce cottons with continually improving properties, faster maturing, increased yields, and improved insect and disease resistance and fibers with greater length, strength, and uniformity. [26]

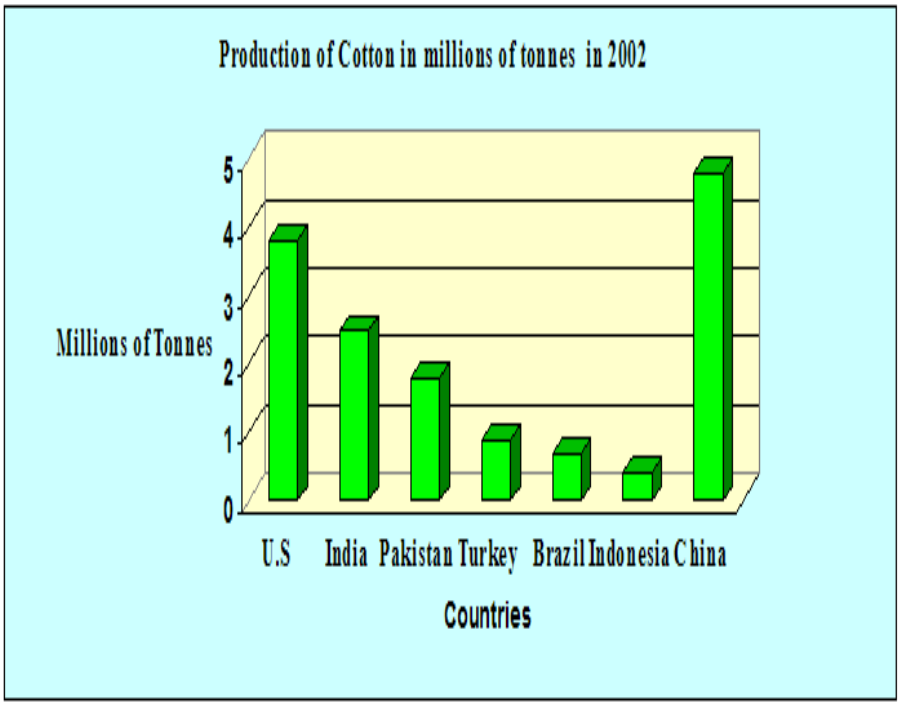


Fig. 1 Development of cotton production in the world [31]

Very serious threat to cotton cultivation are pests and disease. Cotton is attacked approximately by 1300 kinds of pests, so when its cultivation consumes huge amounts of pesticides which are sprayed during the year 1-6 times. These chemicals, however, represent a large problem on the environment in the form of contamination of soil, water, foods, ground water, but can also cause poisoning in any growers. Another factor in the cultivation of cotton is also that in third world countries, there are disastrous working conditions and child labor is used. It is reported that the global crisis in the cultivation of rice, which makes social and political crisis in some countries, is mainly caused using land for the cultivation of organic cotton and other agricultural products. These plots are often a source of energy (sunflower or rapeseed) and grown instead of rice. As is known, the price of oil is now around 108, USD / barrel and is expected to rise further. Therefore, researchers look for renewable energy sources such as biomass and natural oils). Concurrently the cultivation of cotton is also same as other cultivated plants such as sunflower and rapeseed. Today's trend is also to get the energy from the seed cotton. Overall, the largest cotton producer China, (according to CCIC) where 21% of the global area is used for growing organic cotton. The global players in growing organic cotton are the following countries: India, China and South Africa and other 9 countries. Cultivated areas occupy 7.3 million hectares. Genetically modified cotton began to sell on the international market since 1996 and is dedicated to nine countries.

Fig. 2 Preparation of cotton seed in Senegal [2]

The countries that meet the agronomic requirements and allow the cultivation of organic cotton are Australia, China, India, Indonesia, Mexico, USA, South Africa and Colombia. Organic cotton is grown without the use of chemicals and fertilizers. The aim is to preserve the natural cotton integrity and is designed for clothing of children and for people who suffer from allergies to chemicals and is also used in medicine. Rapid development of organic cotton cultivation occurred also in Senegal. In the beginning it was only 53 organic cotton fields from 10 villages, and today the number is around 428 from 104 villages. It should be noted that the number of women producing organic cotton is greater than the number of men in the industry. At the end of each harvest of organic cotton, it is necessary for organic cotton producers to obtain certification. For example, production of the campaign 1995/1996 did not receive the certification in Senegal, not because of failure of technical parameters, but because the campaign 1996/1997 obtained certification in 2006/2007. After the campaign gather all the cotton production in one place and transport to customers for example Enda-prone. The purchase price is 0.34 euro / kg and the storage and sale of organic cotton, of course, depends on the amount grown. Between 1995/1996 and 2000/2001 it was 38.4 tons. Companies Enda-prone and Agro Bio were the first who were involved in organic

cotton farming in the territory of Senegal. Preparation of organic cotton farming starts in April, then growers must choose who must meet the following conditions: In the previous year conventional cotton must not be grown on the plantation.

- It is prohibited to use chemical fertilizers and chemical pesticides.
- It is forbidden to use instruments that were used on the chemical.
- Only use of natural fertilizers, such as wood powder, etc.

It is well advised to prepare the soil, which helps to keep the dry season and continue to have adequate soil moisture and use 30-50kg/ha fertilization to achieve sufficient density (density) of organic cotton.

- Distance between plants should be 30-35 cm.

Furthermore the natural products must be used instead of chemical pesticides. In Senegal some trees were found that are very effective against pests with organic cotton plantations. This is a Neem tree with the Latin name Azadirachta Indica. Other trees are named with the Latin name Khaya Senegalensis. The cotton fields with organic cotton are applied with bio pesticides capsicum, but which due to their cost are not suitable for growing organic cotton. Maturing cotton in Senegal begins from November to January, its storage is a very important process, each package must be properly marked, organic cotton harvest is done by hand, so it is attended by the whole family, on plantations with organic cotton but Babies should not work. The organic cotton is of great interest for the following reasons:

- Price of organic cotton is higher than the price of conventionally grown cotton.
- Debt for growers is smaller, because farmers no longer need to buy chemicals.
- Eliminates the negative effects, such as human and animal poisoning by chemicals and soil toxicity, as well as natural cosmetics, also called organic materials beginning to have a firm place in the shopping area for only environmentally minded consumers. But what really means in the case of bio preposition shirt, towel or baby products. And how to navigate in their marking? Textile industry has long been among the biggest load factors of the environment. Nearly a quarter of all insecticides applied annually is used in the cultivation of cotton. Other significant amounts of toxic chemicals are consumed annually in the conversion of cotton fiber for shirts, towels, bed linen etc. Neither the textile production of other vegetable and animal fibers, nor the complicated chemical processes of 100% cotton, silk or wool, is far from the idea of the nature of natural materials that we recall at first glance. It is not surprising that many people interested in turning to clothing produced a way for nature and man favorable, even in products labeled as "natural", "bio","eco" or "green" textiles, need to be able to measure and define. [27]

Whey comes the name coton in French and cotton in English

Previously called carpas cotton, it is of Greek origin, or carbasus which is of Latin origin, so we know that the name of cotton in French and cotton in English has Arabic origins, the name El Kutn named for very thin fabric. [1]

2.Main goals

As already stated above, the aim of this work is to compare conventional and organic cotton. Analysis was carried out by experiment, for specific properties of both types of cotton fibers. In addition to these analyses it is urgent to have a scientific way how to certify organic cotton, to find a methodology which would identify pesticides in cotton fibers. Thereby contribute to preventing counterfeits, which is presented as conventional organic cotton. This happens in case of 30% of products from organic cotton. This means identifying the cotton impermissible substances (especially pesticides). Analyses should have explanatory power for both raw cotton and cotton products. In practice, the method to distinguish between organic and conventional cotton does not exist.

3.State of art

Unlike synthetic fibers, which are spun from synthetic or regenerated polymers in industry, cotton fiber is a natural agricultural product. The cotton plant is a tree or a shrub that grows naturally as a perennial, but for commercial purposes it is grown as an annual crop. Botanically, cotton bolls are fruits. Cotton is a warm weather plant, cultivated in both hemispheres, mostly in North and South America, Asia, Africa, and India (in tropical latitudes). Mostly it is cultivated in the Northern hemisphere. It is primarily grown between 37′8 N and 32′S but can be grown as far north as 43′8 N latitude in Central Asia and 45′ 8 N in main land China. Planting time for cotton varies with locality, from February to June in the Northern hemisphere. The time of planting in the Northern hemisphere is the time of harvest in the Southern hemisphere. Seedlings emerge from the soil within a week or two after planting, 5–6 weeks later flower buds or squares form, and white (Upland cotton), creamy yellow (Pima cotton) to dark yellow blossoms appear in another 3–4 weeks. The time interval

from bloom to open boll is about 40–80 days. The open boll lets air in to dry the white, clean, fiber, and fluff it for the harvest. Fiber bundle cross-sections obtained with transmitted light microscopy for natural brown cotton where the presence of material bodies are visible within the lumens of some fibers and for natural green cotton where the fibers are quite immature and are characterized by the presence of suberin in the fiber walls and not material bodies in the lumen. [26]

3.1 Parameters seeds and growing conditions pedological organic and conventional cotton

Soils in the region Koungueul city in Senegal, where organic and conventional cotton is grown, is alluvial, sandy, ferric, salty, lithographical leaching.

Type of seed: Genealogy (IRMA 1243 PB * 5) - 32 45-859 E 281-789 F - G 440 company ISRA / Senegalese Institute for Agricultural Research / hybrid 1986th type of pyramid. green-red . The capsule medium, seeds and green. harvest 43.9% fiber (10 saws). Capsule Weigt 3.72 g (ISRA). Used fertilizer type NPKSB(14-23-13-5-1) 200kg/ha, pesticide, 3.7 l / ha urea 30kg/ha [2]

seeds are the same in these fibers: con1, con2, bio1, bio2.

Cotton plant grows in tropical and subtropical conditions, lives a decade and can measure up to ten meter. Cultivation of cotton shows that its size is limited to one to ten meters, to facilitate the collection of cotton and is usually used as an annual plant. During flowering period appear large white or yellow flowers with five petals flowers. For cotton, alternating between wet and dry climate is important for its development, however in the African savanna, where cotton grows, the climate is characterized by wet and dry from April to August. African soil is already rich enough organically, the soil is highly enriched with chemical fertilizers, except that at the end of the growing season, the plants are cut and burnt directly in an area that allows direct recirculation of most nutrients, but also reduces the availability of phosphorus. In African countries with low rainfall, irrigated cotton is the case with much of cultivated land in Egypt and all those of Morocco. In last forty-five years in West Africa, areas reserved for cotton has increased from 1.5% to 3, 5%, this extension of cotton cultivation was accompanied by an increase in yields ranging from 400 kg/ha to 1t /ha. This could lead to the depletion of soil, as well as pollution caused by excessive use of chemical fertilizers. In West Africa, organic cotton appeared a decade ago and is now trying

to organize under the guidance of team manager, however, a study conducted in Mali found mixed results: an increase in productivity, the competitiveness of organic cotton. Africa has unfavorable risk of flood, which changes soil fertility required for cultivation of organic cotton. The global market for organic cotton fiber is a very narrow niche market. Organic cotton is a niche market with global production of 32,535 tons of fibers exceeding 23.4% compared with demand of Africa, which is 865 tons. Cultivation of organic cotton with natural fertilizer comes from various sources. In Mali, a country park is the most common source and the richest in minerals, especially potassium. However, their development requires a litter of straw-based cereals, these residues play their longer protective role against soil erosion [26]

3.2 Taxonomic inclusion of cotton

Empire	plants (Plantae)
Vascular	plants (Tracheobionta)
Department	Angiosperms (Magnoliophyta)
Class	higher dicots (Rosopsida)
Order	(Malvales)
Family	(Malvaceae)
Rod	(Gossypium)

3.3 Composition of cotton fiber

The content of some substances depends on the soil where cotton was grown and the possible attack by pests.

Composition of cotton[27]

Cellulose	88-96%
Pectins	0.9 to 1.2%
Protein	1.1 to 1.9%
Wax	0.3 1%
Organic acid	0.5 - 1%
Mineral	0.7 to 1.6%
Sugars	0.3%
Others	0.9%
Metal	ppm
Potassium	2000–6500
Magnesium	400–1200
Calcium	400–1200
Sodium	100–300
Iron	30–90
Manganese	1–10
Copper	1–10
Zinc	1–10
Lead	n.d.
Cadmium	n.d.
Arsenic track	(<1%)

Also of potential concern is the presence of arsenic-containing compounds, which are introduced primarily through agricultural practices such as harvest aid products (arsenic acid) and post emergent herbicides Arsenic acid is no longer registered for use in the United States, and organic arsenic containing post emergent herbicides are used in less than 4% of the U.S. cotton production and are being phased out. While these compounds are generally removed

through the scouring process, their presence may be of some concern for both health and marketing reasons. For solid waste, such as textile mill fiber waste (e.g., undercard and pneumaphil waste), the U.S. Environmental Protection Agency (EPA) has established limits for the leachable metals from the waste. If these levels are exceeded, the waste has to be treated as hazardous. Cotton does not normally contain any metals in sufficient quantity to be of concern and therefore, if the cotton fiber is not recycled, it can be disposed of in normal municipal landfills or lined landfills. Some textile mill carding and other yarn manufacturing wastes are presently used as animal feed, which indicates that yarn manufacturing fiber wastes have no or very low toxicity and are generally regarded as safe. [7].

Fig. 3 Medieval tree of cotton [26]

3.4 The growth of cotton

Growing cotton was one of the main economic activities of the first colonists in the Well-profit world. The first mention of cotton colonists is from 1556, since when it was grown in Florida, and in 1607, since when it was grown in Virginia. The real time when cotton became the most important source of textile fiber was the industrial revolution in the second half of the 18th Century. In the 18th Century cotton yarn spinning machines in England were first used which were soon driven by other invention of Watt engine. In 1764 incurred machine for spinning yarn spinning Jenny in Blackburn in north-west England, that made possible further processing of cotton efficiently in 1497. Englishmen got from Vasco-de-Gama clothing made of cotton, sparking complaints traders with wool and cotton export

was banned and ordered that the man, who dresses in cotton, must pay tax. It was from 1700 and it took about 36 years before the tax was abolished and France emperor Napoleon demanded payment of tax on clothes made of cotton. Cotton is grown in one hundred countries in the area of 36 million ha, i.e. 2.5% of the world agricultural land and global scale cultivation of cotton now helps 350 million people to work (production, transport, storage, etc.) Regardless of the services associated with cotton seeds germinate after a week from cultivation, a system, where cotton grows further; it needs a lot of water. After a month, flowers grow up to 15 cm, flowers are left to continue to grow only from planting to mature cotton elapsed time in the range from 140 to 230 days, depending on the species of cotton. Cotton can live 10 years in natural environment, while grown for 5 months.

Fig. 4 Flower of cotton [3]

Flowered from 40-60 days, after seeding the yellow color arises and if color is purple, it is followed by the formation of capsules. But during drying, it leads to ring opening and the consequence is layer on the fiber surface, 20-30 days are needed for bloom, 45-70 days after removal of the flower, capsules grow and cotton fiber capsule consists of 3-5 cases in each seed, 13-20 days are needed for growth of primary wall, 25-40 days are needed for growth of secondary wall. Cotton needs plenty of water, heat and unwavering compliance with other

agronomic standards. It is sensitive to changes in humidity, (65% +/- 2%) as it leads to a change of strength and elongation; humidity affects dissolution and breach of hydrogen bonding, followed by stress relaxation (deformation).

Fig. 5 Cotton plantations [3]

Fig. 6 Ripe cotton [2]

3.5 Problem with cotton growing

There are two kinds of problems in the area of cotton in developing countries:

- Those that relate to the fundamental problems of developing countries
- Those that relate to international markets

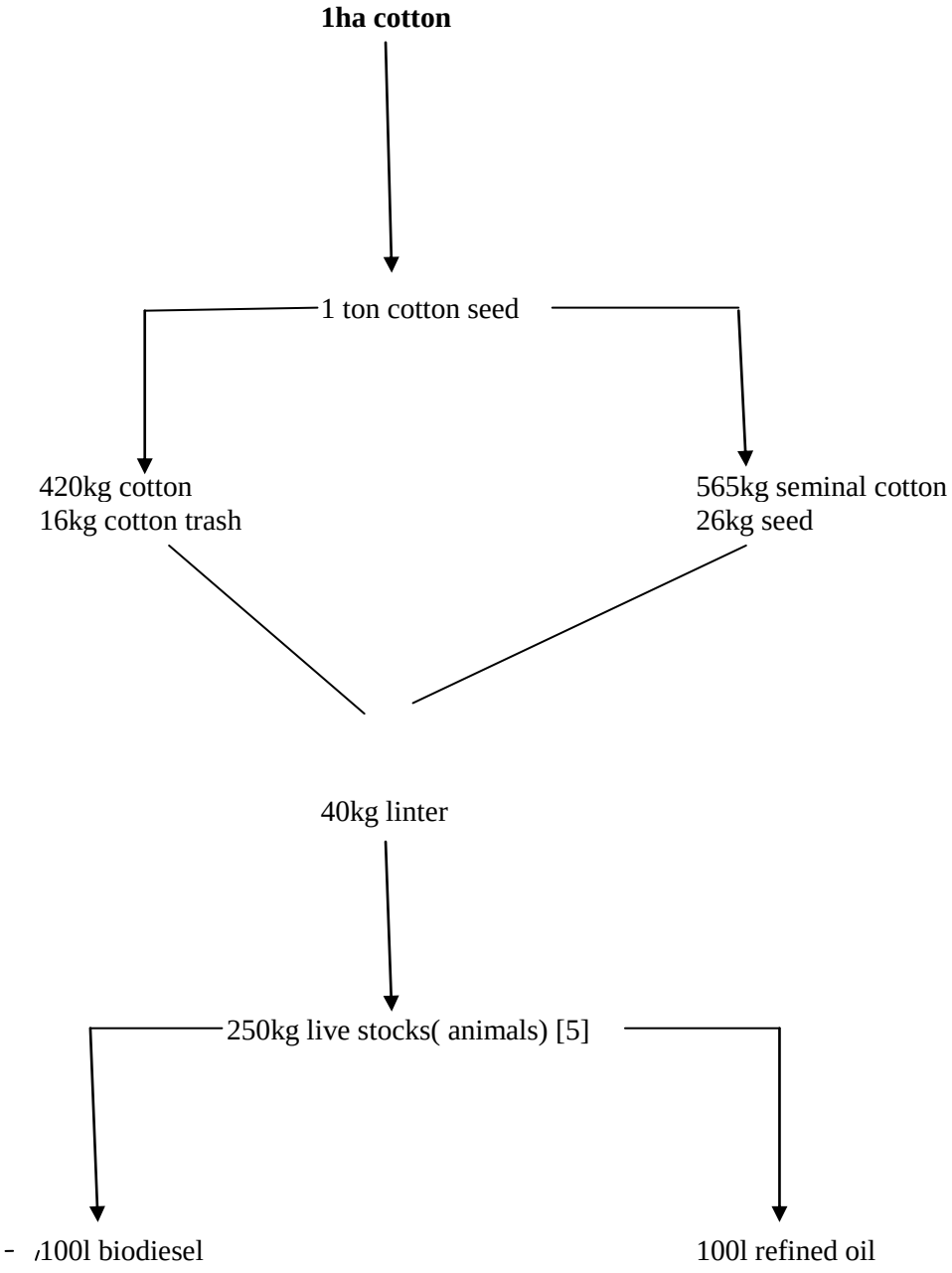
It can be said that the problems that occur in the cultivation of cotton, they are only a reflection of the problems of developing countries:

- Unclear government policy in the development of cotton production (land, taxes, etc.)
- Outdated equipment and technology
- The cultivation of cotton only in the rainy season
- No financial subsidies
- Lack of financial structure (bank) to support the cultivation of cotton and the necessary funds, as banks require guarantee
- File agronomic problems, labor and management in cotton

Issues that relate to international markets within Senegal's control, primarily by financial subsidies that farmers receive from other countries such as America and European countries,

such as China allows those farmers who are unable to gain the harvest that will return the money invested in cotton, another problem is that the sale price of cotton is determined by certain parameters. Senegal as well as other developing countries don't have the opportunity to influence other problem is the currency of sales, which is in USD since 1866, and no one is yet able to change. Immigration of cotton farmers towards the cities and to neighboring or developed countries is also a problem, nowadays, most farmers focus on growing organic plant, but this also partly influences part of the land which is devoted to growing such turnsole (flowers from the sun). Because cotton cultivation in Senegal depends only on the rainy season, it is also a big problem for the development of cotton, oil price and tax on exports of cotton and supplies for planting are also important reasons of these mentioned problems, one must not forget the environmental problems and various types of insect pests, 1300 kinds are registered. The existing 500 kinds on the African continent are the most famous types of Aphis gossypium that harm the cotton plantation, destroy the quality of cotton and cause the formation of substances like niello. Cotton growing and processing, however, in no way inferiors to environmentally most problematic agricultural and industrial chemical residues. Difference around cotton fields and their accumulation in the tissues of living organisms, including humans and livestock can not be effectively prevented. Many pesticides belong to the highly toxic substances such as aldicarb to disinfect the soil or endosulfan to protect cotton plants from pests, it can have fatal consequences for the lives of many farmers and their families in developing countries, as one can buy some of the substances that are in America and Europe, long banned by legislation. Pest control pesticides are employed to remove weeds and foliar herbicides and desiccants. Pest control in cotton cultivation is carried out in different regions according to different needs and climate conditions. On a global scale, about 20% of pesticides are used to grow just cotton.

Everything is good in cotton



3.6 Critical evaluation of the literature and overview of the current situation

If cotton can be considered as one of the fibers, which accompanies man throughout life, with the emergence of organic cotton a very serious problem emerges for some experts who have a very suspicious vision or a very simplified analysis of organic cotton. That is to provide kit for the detection of pesticides on cotton , methods based on electrochemical using bio sensors ,algae with ultra sound extractor, using FT-IR, which does not give a complete solution for the detection of pesticides. Choosing organic cotton is to contribute to the preservation of our health, especially for children; cotton consumes huge amounts of pesticides that are applied in the range of 5-10 times than other vegetables. But these chemicals are great problem on the environment in the form of contamination of soil, water, food, ground water etc. Another disturbing factor in the cultivation of cotton is also that in third world countries, job and work conditions are disastrous and child labor is used. Certification of organic cotton is done at present under the same cultivation conditions. Some argue that simply pesticides do not exist on cotton as confirmed Institute at Bremen, Germany or BVT BRNO. In 2009 during a visit to TUL in recommending us to do tests on pesticides immediately after harvest or on cotton, based on their tests on samples of cotton from Senegal, but under the proposed detection methodology. This can detect chemical pesticides. Type of pesticides and pesticide tests were conducted also with the old cotton samples (15 years) of cotton (Syria, Egypt, Indie). It can be confirmed that there is no trace of pesticides on cotton fiber, the methodology developed in this work, today confirms that this method can detect pesticide for cotton, gives a chemical name. and chemical formula of the pesticide.

3.7 Used devices

Using devices, which are available at the Faculty of Textile TUL, some of the majors properties of cotton fibers e.g. mechanical properties of cotton on Labor test bond strength with the device Pressley Tester, maturity using a polarizing microscope, using the apparatus micronaire for fineness, staple diagram for length, the thermal properties with the differential scanning calorimetric (DSC) and TGA and physical chemical properties by the analysis of gas chromatography with mass spectrum Varian 3800/2000 were done. These methods: GC / MS instrument for gas chromatography helped to find out the presence of pesticides in samples of the conventional and organic cotton.

3.8 Methodology and working practices

The main properties of cotton fiber have been investigated using devices at disposal in the textile faculty and in the technical university TUL.

3.9 Geometric properties of organic and conventional cotton

An accurate knowledge of the geometric properties of textile fibers is essential to select the proper fiber for specified textile end use applications. However, to have meaningful comparisons between fibers, experience has shown that it is necessary to conduct measurements under known, controlled, and reproducible experimental conditions. These include mechanical history, relative humidity and temperature of the surrounding air, test or breaking gauge length, rate of loading, and degree of impurities. Mechanical history is important because fiber could be annealed, extended beyond its elastic limit, or otherwise affected by mechanical manipulation

3.9.1 Length with staple diagram

The basic graphical representation of cotton fiber staple diagram was done. A thread of unit length, and its length is defined as the distance fiber ends without arches and tension. Especially for cotton, this property is one of the important parameters in evaluating quality. Also, it is taken into account when blending cotton with other fibers. Since it is a natural raw material, the individual cotton fibers of different lengths are not uniform, unlike synthetic fibers.

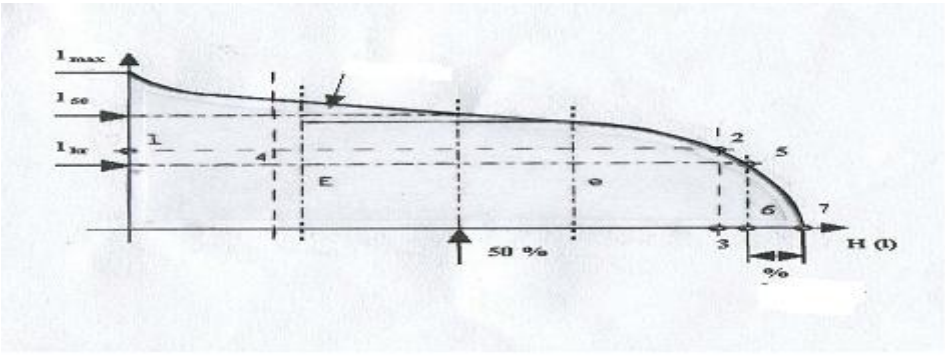


Fig. 7 Figure analysis of staple diagram [28]

On axis x H(I) –Probability occurrence of fiber length longer than l

On axis y Length l

The graphical analysis of staple diagram is based on the point 1. It is found by calculating the relation with point 2. After the point 2 in the diagram it leads parallel to the axis H (I). After crossing the line to the curve is reached staple item 2. It is constructed from a point perpendicular to the axis of H 2 (l) and subsequently obtained point 3 at a distance of 0-3 lines perpendicular is erected, and its length is plotted point 4. From there, it is again parallel to the axis D (l). It is intersecting the curve created by staple diagram. Then, running perpendicular to the axis of H (l) section 6 is plotted. At a distance of ¼ is the effective length. Distance ¾ from is the effective length; the small difference between the two is called the effective lengths. Samples of organic cotton and conventional cotton were tested. First, the fibers in flake settled on a common base in the comb box, then, after lengths (5 mm), it was pulled. This line forms an imaginary axis x. First it was the longest fibers being pulled, then shorter and shortest to last. Around lengths aligned fibers was traced curve staple diagram. The x axis shows the number of fibers, respectively likelihood of fiber length H (l) and y axis shows length.[28]

3.9.2 Maturity with polarized lighted microscope

Maturity of cotton fiber affects the fundamental properties such as fineness, and some mechanical properties. One of the methods for the assessment of maturity cotton material is the method of polarized light according to norm CSN 80.

Measuring principle:

When using a polarizing microscope, working with a red background in third order plate included R3, birefringence, and the characteristics of cotton fibers on the basis of interference colors. The content of the mature, and dead polarized fiber maturity and the number and class of ripeness was determined.

How to measure

The raw material is cotton after combing, which removes fibers shorter than 10mm. Leveled parallel fibers are inserted without immersion into fluid between two glass slides. The preparation is placed on a glass microscope in the field of view around the midline of the preparation. Preparation is in the lateral direction, while the count of fibers is done for those, which appear in the visual field of the microscope. Then summed mature fibers in the specimen are retracted and while moving in the original direction the number of dead fibers is counted. The detected amount of each maturity groups is recorded separately. In all three cases, the testing is performed in the same line. Mature fiber: the fiber, which in a polarizing microscope visual field, looks light green color along its entire length, or more than one half of the length.

Dead cotton: fiber, which is an exemplary field polarizing microscope, shows basic red with no green tint for its entire length. Production of mixed fiber: not counted, their number is determined as the difference between total fiber N and the sum of mature fibers .Equipment and tools for measuring:

1. Polarizing microscope with cross wire preparation, lighting lamp
2. Tweezers, scissors, needle
3. Spiked comb
4. Slides

Preparation for Mature fiber content:

Polarized and dead fibers are a percentage of the number of fibers in each group. The result is expressed to two decimal places. For comparison of the test results and the inclusion of cotton maturity class number is calculated with following formula:

The formula for the calculation of maturity

$$c_z = \frac{(3.0\,N_m)+(1.5\,N_{mm})+(0.5\,N_d)}{N} \qquad (1)$$

N	Total number of cotton fibers
N_m	Number of mature fibers
N_d	Number of dead cotton fibers

N_{mm} Number of medium mature cotton fibers

Table. 1 Maturity according to standard CSN 800311 [5]

3.9.3

CLASS OF MATURITY	DEGREE OF MATURITY	CONTAINED MATURE FIBER [%]	NUMBER
I.	Very good mature cotton	85 & more	2,75 & more
II.	Good mature cotton	75 – 84,9	2,50 – 2,749
III.	Mature cotton	70 – 74,9	2,40 – 2,499
IV.	Immature cotton	60 – 69,9	2,20 – 2,399
V.	Medium mature	50 – 59,9	2,00 – 2,199
VI.	Immature	less than 50	less than 2,00

Measurement of fiber fineness

Fineness was determined by the value of micronaire. Measurement of fiber fineness of cotton is different from previous models containing both receding front tube manometer and flow, this device is also equipped with a calibrated scale that allows direct reading of the observed values. Fiber fineness is measured by varying the air flow resistance, the pressure indicated on a scale number is (MIC micronaire). A sample of cotton fiber with a defined mass is compressed to a certain volume, the air passes through the sample and the flow rate steady pressure indicates micronaire value.

Weight 5g sample with an accuracy of ± 10mg was taken. The measuring device must be well adjusted and calibrated to measure the cotton correctly.

Measuring procedure

Weighed 5 g sample of cotton was put into the measuring chamber so that the fibers were preferably distributed, the lid was attached and the chamber was closed. Then the air valve is closed and device may be started, then slowly the valve was opened until the liquid level in the tube falls to the bottom of the scale, then the value of the micronaire (MIC) was noted, which corresponds to the upper blade float, average micronaire was calculated and the conversion to the fineness [dtex] was made according to the formula: [5]

$$T = 0.437 \cdot MIC \qquad \text{[dtex]} \qquad (2)$$

From knowledge of the volume and weight of cotton bundle, the relative of the PI F[cNtex^{-1}] [5]

3.10 Mechanical properties of organic and conventional cotton

Mechanical properties of materials are generally their response to external forces. Mechanical properties are applied in the processing of fibers and, therefore, are included among the processing properties. According to the above definition, the mechanical properties of fibers appear as a response to mechanical stress on fibers through external forces. These kinds of stresses usually occur in combination (tension - compression transverse to fibers in the yarn twisting). This laboratory strain was examined separately, and is the only standardized test of tensile strength. During mechanical stress in the fiber, the shape has to change or deformation occurs. For mechanical stress, was employed Labor-tech design with the Open max test force 1N. This device is intended for mechanical tensile tests of individual fibers. The device Pressley tester was used to measure bond strength of fibers. The advantage of measuring bond strength is that it provides information on the average fiber strength of cotton. The device micronaire and Pressley Tester are included in the HVI methods. [5]

3.10.1 Testing of bond strength on the device Pressley Tester

Testing the strength of the individual fibers is very time consuming. For a fast decision when buying raw materials, while blending in technology and quality assessment of raw material was necessary to find a fast and reliable method that would meet these requirements. One of such methods is testing the bond strength in fibers by Pressley Tester. The method is to create a file assembled fibers, breaking volume, its subsequent consideration and calculating the strength characteristics. A small amount of cotton fiber settles in parallel position as a thin bunch is clamped into the jaws of the instrument. Jaws are arranged next to each other like a pair of complex jaws. After placing the fiber bundle into the jaws, they closed and tightened, it happens in a special torque device, which indicates the correct strength. After removing the jaws of the device, the protruding fibers are cut off. Break is caused by traversing weight lever that decreases the weight at break and stops. Then the jaws

are removed from the device and the fiber bundle is opened and weighed on precision scales in [mg].

Pressley index PI:

$$PI = \frac{F\ [lb]}{m[mg]} \qquad \text{[lb/mg]} \qquad (3)$$

Pressley Tester instrument is included in the HVI method [5]

3.10.2 Testing strength and fineness cotton fiber with Apparatus Vibrodyne / Vibroscope 400

Individual fiber material was first measured on the device Vibroscope 400 where the fiber fineness was measured in $cNdtex^{-1}$ and based on the information on the fineness appropriate voltage was selected for the second part of the test to be performed on the device Vibrodyne 400 and to determine the strength and elongation of fibers.

3.10.3 Dynamic mechanical analysis (DMA)

The principle of the device DMA DX04T is mechanical stress on the sample as defined by force and the deformation response at a given temperature and time. The assessment of the strain waveforms and the deformation can be obtained according to the modulus of elasticity and loss angle on temperature and time, frequency of the applied force, etc. The magnitude of deformation curves obtained is used to determine the characteristic properties of a material.

Principle of measurement:

In dynamic mechanical testing of the sample alternating stress (sinusoidal or other course) was applied, and the resulting voltage was measured. For solids that behave ideally, or at least in the small deformations which behave according to Hooke’s law, the resulting strain is proportional to the amplitude of the stress and tension and stress signals are proportional to each other. If the sample is liquid, and if it behaves ideally, then the voltage is proportional to the strain rate (Newton's law). In this case, the stress signal is in phase with the strain signal,

but out of phase advancement at 90°C. The voltage signal generated with elastic material can be resolved into two components. Elastic tension real part E′, which is in phase with the strain, and the viscous stress imaginary E′′, which is in phase with the strain rate (assessed at 90 °C have been provided against stress) These two components simultaneously material dependence on the amplitude of the stress and strain rate can be measured. Elastic and viscous stress depends on the material properties.

Viscosity

$$\eta^* = \eta' - i \cdot \eta'' \qquad (4)$$

Dynamic test modes

For dynamic test control oscillation frequency of oscillation amplitude and frequency rheometer temperature performance was used. In a typical test two of these parameters are maintained at a constant level, while the third parameter is continuously varied. The basic test is sweep deformation, frequency, temperature, time and duration of hardening, where sweeping means smooth changing of the parameter in the actions selected by the test engineer. Rheometry still offers multiple frequency current mode and the mode with an arbitrary waveform course. The values of the physical properties of fibers are altered during dynamic stress and at different temperatures. This is a result of visco elasticity, defined as the time-dependent mechanical deformation. During the dynamic stress, strain and deformation is described by relationship:

$$\sigma(t) = E(t) \cdot \varepsilon(t) \qquad (5)$$

$$E(t) = \frac{\sigma(t)}{\varepsilon(t)} \qquad (6)$$

Where: σ(t) is the strain

ε(t) is the deformation

The resulting modulus, a measure of the total resistance of the material to deformation, can be calculated from the following equation:

$$E^* = E' + i \cdot E''$$ (7)

Where: E´ Elastic (real part) modulus

E´´ Loss (imaginary part) modulus.

The proportion of Loss modulus to elastic module is the tangent of the phase shift between strain and stress. The following applies:

$$\frac{E''}{E'} = tg\,\delta$$ (8)

Where: δ loss angle.

The resulting viscosity can also be calculated from the relationship

$$\eta^* = \frac{E^*}{\omega}$$ (9)

ω angular velocity [radian S^{-1}]

The use of DMA

DMA can be used to characterize polymeric materials and the modulus dependency (loss angle), the temperature (or time). DMA provides basic and necessary data on the mechanical properties of polymeric materials, which are directly related to their processing.

Measurement procedure

Samples of fibers were placed in a paper box on a 1 x 1 cm, which allowed for better clamping of the sample into the instrument. Using the DMA to identify the initial modulus of elasticity of samples and for setting various parameters in the DMA, the measurement was started.

Modulus of elasticity

Force curve sinus

Manner of note insertion forces - measurements with constant force

Measuring mode- thermal scan,

Force amplitude max -200 mm, min.300 mm

Deformation limit 2 mm

Frequency 1 mHz

Temperature 180 ° C, room temperature 30 ° C

Heating rate 3 ° $C.min^{-1}$

3.11 Electrochemical sensors for the detection of pesticides in conventional and organic cotton

Electrochemical sensors with immobilized enzyme acetylcholinesterase (ache) are used to identify inhibitors of ache. Among ache inhibitors are currently organophosphate and carbamate compounds (pesticides, chemical warfare agents). Measuring principle is enzyme substrate reaction such as inhibitor (in this case a pesticide) on the active site of the enzyme. The measuring method is I=f (t) dependence of current on time). If the sample contains ache inhibitor, pesticide, then the measured response curve and substrate changes the direction.

3.12 Scanning electron microscopy of conventional and organic cotton

The invention of the scanning electron microscope is known for quite a long time. It is applied in many scientific disciplines and among its main advantages is calculated possibility of direct observation of the object impervious to electrons, a simple preparation of specimens, high resolution and magnification range, excellent depth of field and the plasticity of the image. Early research and development of scanning electron microscope (SEM - Scanning electron microscopy), it is placed in the 20th century, when it was launched in the research laboratories of the University of Cambridge in England. In 1965, the world first saw the light scanning electron microscope STEREOSCAN at Cambridge. In the Czech Republic, production of these devices began in 1976, when it was brought to life by scanning electron microscope TESLA BS 300th All these devices operate under high vacuum. Activity scanning electron microscope is based on a narrow beam of electrons emitted from the cathode filament and accelerated in electron nozzle system comprising a cathode Wehnelt s cylinder anode. The beam is further processed by electromagnetic lenses and is swept over the surface of the observed object. Synchronously with the electron beam is swept electron beam in the observation screen. The interaction of the electron beam with the surface of the observed

object creating secondary electrons (along with photons, reflected electrons etc.). These detection after amplification and modulation generates the brightness of the electron beam in the observation screen, so the screen image is created corresponding to the observed surface of the sample. Resolving power of the microscope is given by the equation.

$$\Delta = \frac{\lambda}{n \sin \alpha} \qquad [\text{nm}] \qquad (10)$$

where λ is the wavelength of the radiation [nm] and nsinα the numerical aperture

$$Z_m = \frac{d_o}{d_p} \qquad [\text{l}] \qquad (11)$$

where the Z_m magnified microscope, d_o[m] is the screen resolution, d_p [m] resolution is related to the subject.

Where the d_o [m] is the screen resolution, related to the subject. Useful magnification of microscope is based on the order of 10^3 - 10^4. As already mentioned, classical SEM works with minimum vacuum of 10^{-2} [Pa], and therefore, a special slide preparation is required, especially metal. In many cases, it's not just a mere object. In this context it is necessary to know the accuracy with which it is possible to measure geometrical dimensions at high magnifications. Analysis showed that the maximum relative error varies with the classic SEM (Tesla BS 300) in the range of 5.53%. Manufacturers of electron microscope pay considerable attention at present on apparatus, which can be placed to observe the sample at a higher pressure, e.g. 300 Pa. Applied pressure is limited by the type of detectors. These scanning electron microscopes are known as environmental (ESEM). The advantage of these devices is the ability to observe biological samples and insulators without complicated preparation.

Principle of SEM

At each point of the sample is a narrow focused beam of electrons (though it scans line by line). The incident light interacts with sample material and forms detectable components. As the beam travels through the sample, the scan varies according to the nature of the surface. The level of the signal detector is then compiled to form the resulting image, and a monochrome image is built.

Electron tube

The source of electrons is an electron gun, usually tungsten filament, placed in the wehnelt s tube, electrons are accelerated towards the sample till a voltage (typically 0.1-30kv) is reached. Volume of electrons (beam) is edited, focusing electromagnetic lenses. Tube usually contains one or more lenses, objective lens, grids and deflection yoke coils etc. Impact of electron beam pattern causes emission of secondary electrons from the sample, which are then analyzed and detected.

Important concepts

Zoom-creates larger or smaller images using the scanning beam deflection coils, at working distance where the beam is focused. Flow in the track current (number of electrons) incident on sample tracks beam diameter at the impact on sample resolution the ability to distinguish two points (approximately half track). [24]

Organic and conventional cotton samples were viewed under a scanning microscope SEM (Scanning electron microscope) VEGA TS 5130 high vacuum microscope, operating at a pressure of 5 to 10^{-3} Pa, used for observation of surface materials in large magnification with great depth of field. The maximum resolution is 3.5 nm. The program is used to display the picture resolution 512 x 512 pixels.

Measurement procedure

Random fibers that formed a smaller volume were glued to the double-sided adhesive tape, laced on a circular metal carrier. Fibers have been secured at the edge of carrier tape, overlapping part of the fibers were cut off, thus samples were prepared using device SCD 030 and inserted into the working vacuum chamber of SEM.

3.13 Thermal properties of organic and conventional cotton

Tab.2 Principles of measurement using TGA, DSC, DMA

Method	Used for example
DSC	Transition temperature, melting temperature effectiveness of antioxidants.Transition temperature, enthalpy
TGA	Thermal and oxidative stability, efficiency, flame retardant
DMA	Mechanical properties modules in tension and shear

The aim of the experiment is monitoring the thermal response of materials. It is often used in combination with thermo-analytical techniques to obtain more additional results. In analysis it is necessary to monitor a number of factors influencing the results. Among them are: Calibration and comparative characteristics of the sample by treatment for analysis.

3.13.1 Differential scanning calorimetry DSC

In this method, the sample temperature is maintained constant for comparison. The amount required to maintain isothermal conditions, is calculated in relation to time or temperature. Thus the measured temperature differential gives the electric power required to maintain isothermal conditions. The amount of heat released is proportional to the amount of electrical energy consumed by heating the sample. It is therefore a calorimetric method. Thermal properties were obtained using differential scanning calorimetry (DSC). Measurements were carried out on a DSC from Perkin Elmer in a nitrogen atmosphere and the cooling brands Minichiller CC. The device operates on the principle of endothermic or exothermic behavior of the sample material. Measurements were performed at the program settings for cottons:

2.0 min isotherm at 25.00 ° C

Heated from 25.00 ° C to 250.00 ° C at 15.00 ° C / min

Cooling from 250.00 ° C to 25.00 ° C at 15.00 ° C / min

Thermal properties of textile fibers are very important. It plays a major role in the selection of suitable parameters during processing and use. It is affected by the chemical composition of the fibers and their supramolecular structure.

3.13.2 Thermo gravimetrical Analysis

Briefly thermo gravimetrical (TG) is a thermal analysis that quantitatively monitors the change in weight (increase, decrease) in the sample. In a static arrangement, it assesses the instantaneous mass w versus time t at a constant temperature (isothermal):

$$W = f(t) \qquad (12)$$

The temperature T is available for most commercial instruments based on linear function of time

$$\frac{dT}{dt} = K \qquad (13$$

So

$$T = T_0 + K \qquad (14)$$

Measurement

Apparatus for TGA, called thermal weight are very accurate scales currently based to equilibrate principle, change in sample weight is offset electromagnetically and thus easily recorded. Structural arrangement can in principle be of two types, horizontal or vertical (more often). Each type has its own advantages and constructional complications. Construction equipment must work under the permitted atmospheres. This measurement gives thermo gravimetric curve which indicates instantaneous mass of the sample in dependence on temperature and time. The shape of the curve is influenced by the heating rate. The higher the heating rate, the narrower the temperature range within which there is change in weight .Thermo gravimetrical investigates weight changes that occur in the material under controlled heating and defined gas atmosphere.

3.14 Detection of pesticide in organic and conventional cotton using gas chromatography GC / MS

As mentioned earlier, there are many chemicals in large quantities, which are not friendly to the environment, but also hazardous for people, their use is accompanied by the international Stockholm Convention. It is a legally international agreement that aims to reduce and completely prohibit the manufacture, use and release into the environment of harmful chemicals. The Convention was signed on 23 May 2001 in Stockholm, Sweden after several years of negotiations under the auspices of UNEP (United Nations Environment Program environment).

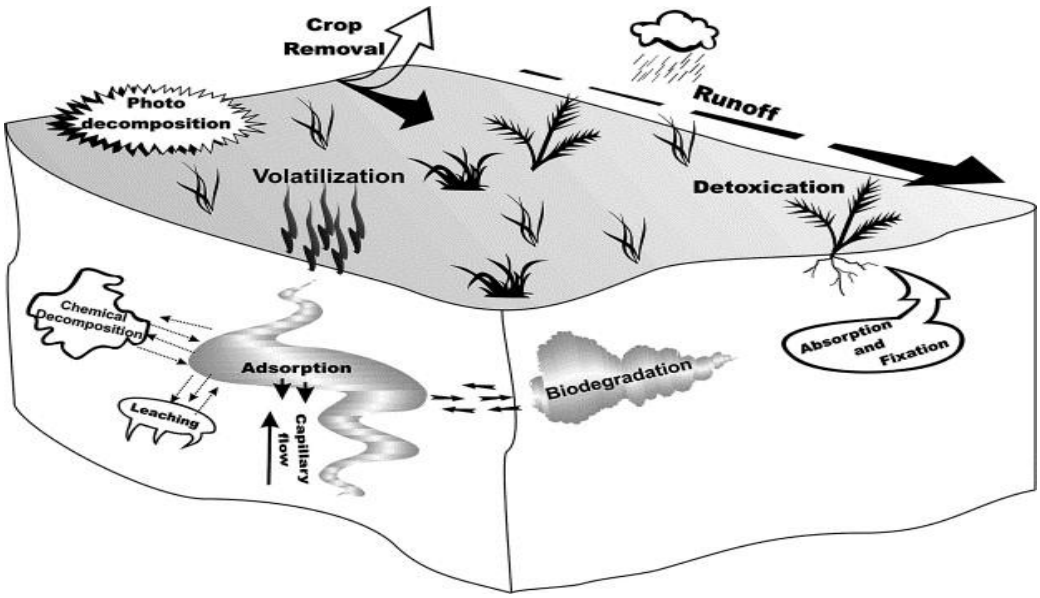


Fig.8 Pesticides residues in soil [29]

Gas chromatography with mass spectrum GC-MS VARIAN 3800/2000 was used. The CP-8400 Auto sampler is controlled by 3800 and will not appear as a separate module.

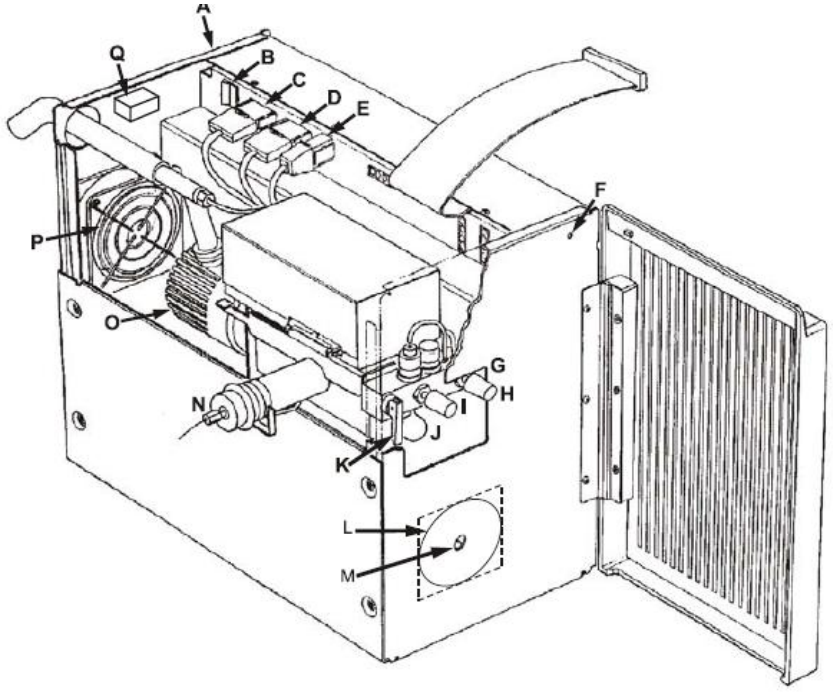


Fig. 9 Gas chromatography spectrum Varian 3800/2000. [20]

D	Trap heaters	B	Service Switch
E	Fuel distributor	C	Transfer line heater
K	Valve	L	RF coil
F	LED	M	RF coil screw
G	Tire Manifold	N	Transfer line
H	Gas	P	Cooling
I	Gas	Q	Shut off valve

Saturn 2000 GC / MS mass spectrometer

Physical chemical method is based on determining the mass of atoms, molecules and their fragments after transfer to the positively and negatively charged ions. It is an ideal method for finding the chemical structure of pesticides present in cotton fibers. Gas mobile phase is used here only for analysis and effects on the stationary phase. GC-MS characterizes especially effective and rapid separation of complex mixtures and works with small amounts of samples, using relatively simple equipment. Gas chromatography with mass spectrum retains priority status for the analysis of pesticides. There is requirement of a high selectivity of the separation process, the separation should occur as little as possible to analyze ions, at present, gas chromatography with a mass spectrum is widely used. The combination of GC-

MS represents a very promising combination of effective separation method with highly sensitive detection used in the detection of pesticides in cotton samples from Senegal, from Egypt, Russia and Indie. Auto sampler is placed on top of the GC capillary column of fused silica. GC converts directly to the assembly line, in ion traps, where the samples are introduced or injected either manually or by using the auto sampler. The following figure shows the block diagram of measurement:

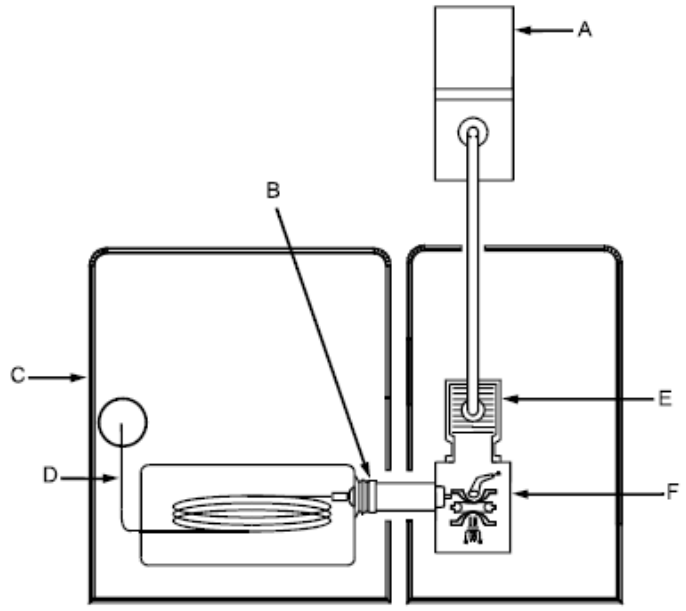


Fig. 10 Scheme GC Varian 3800/2000 Saturn 2000 mass spectrum Saturn 2000 [20]

A vacuum pump, B interface unit, gas chromatography, capillary columns D, E Turbo molecular pump, F ion trap

Tab. 3 Main patterns of gas chromatogram

Gas velocity	$\frac{l}{t} = v$	Gas delivery rate is specific for each column t is time l is length column
The phase ratio ß	The phase ratio β $\beta = \frac{V_g}{V_S}$ $\beta = \frac{r}{2d_f}$	β is phase ratio of the film thickness in stationary phase Vg is volume in the mobile phase Vs is volume in stationary phase r is internal radius d_f is film thickness column
Partition coefficient	$K = \frac{C_s}{C_g}$	C_s is concentration in the stationary phase Cg is concentration in the mobile phase
Capacity ratio K	$K = K' \cdot \beta$ $K' = \frac{t_r - t_0}{t_0}$ The Capacity Factor $K = \frac{t_r}{t_0} = \frac{t'_r - t_0}{t_0}$	This dead-time is t_o Retention time is t_r

Methods of measurement

Method consists of choosing values for the temperature column, respectively. Column temperature program in the section column, injector temperature to injector section, temperature sensitivity and range detector to detector section.

Activation methods

Stabilization of required parameters is indicated by a green LED ready when it is ready for analysis.

Analysis

If the equipment is ready, the sample is dosed during the spraying and test is started automatically by the set program and data is collected. In order to terminate, after the implementation of the selected temperature, the unit automatically goes into a not ready state, and after setting the initial conditions for the analysis an alarm status can be seen for further analysis.

GC Parameters

Advantage Auto Varian CP-3800:

• Removal of application and time for analysis

• Column switching, and easily manipulated by injecting a sample on one or more valves

Configuration

When responding quickly to EFC valve configuration. is optimized for Injectors

• 1079 PTV injector

Column

Quick connect for easy installation, Star Chromatography Workstation

• Simple interface for easy creation and data collection

Operation

Easy viewing with 11 lines and 35 characters / line LCD screen

• Fast GC status display and modification of parameters of the GC

Keyboard

Complete editing method and GC keyboard control

Saving time with instant access to one of the eight methods stored

All CP-3800 GC function

Navigate CP-8400 auto sampler provides high throughput with a standard sample. CP-8410 auto injector provides flexibility with a fixed cylinder to 2 ml, 5 ml and 10 ml. Minimizing errors and reducing costs [22]

GC

Gas chromatographic method is used for the separation and determination of gases, liquids and substances. The method is based on the distribution of components between the two phases, the mobile and stationary phase. In gas chromatography, the mobile phase is a gas, called the carrier gas phase and is placed in a chromatographic column. The stationary phase in packed bed columns can be solid (activated carbon, silica, alumina, polymeric adsorbents, etc.). Each component of the sample through the column progresses on the distribution component and the equilibrium concentration of the component in old stationary and mobile phase occurs. Gradually deposited on the column in order of increasing values of distribution constants and enters the detector.

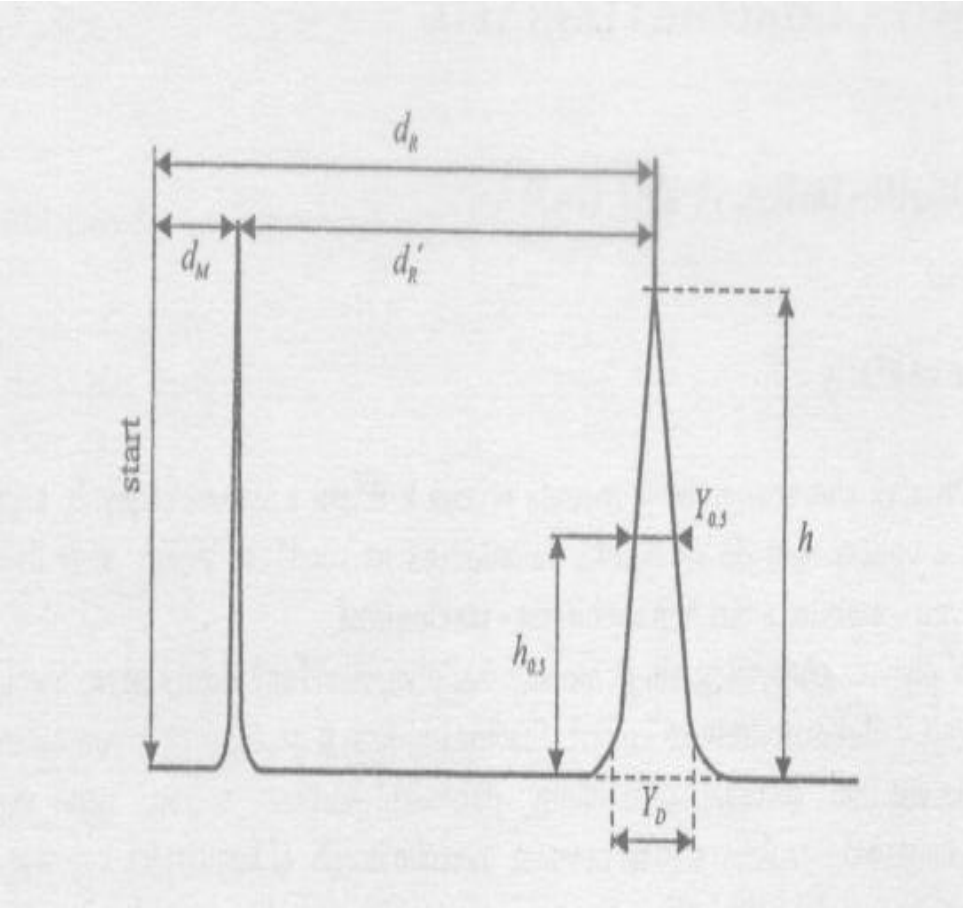


Fig.11 Retention parameters [19]

Retention distance dr. [cm] is the distance to the beginning of the chromatogram and the maximum peak by spraying the sample on the column. The retention distance can be easily involved about retention time and retention volume. Retention time tr [min] is the time of passage of the substance through the column to the time from the injection of the sample on the column to reach the peak. The retention time can be calculated from the retention distance dr and speed shift registration paper S [cm min^{-1}], when using the recorder.

$$S \cdot d_r = t_r \qquad (15)$$

The retention volume V_r [ml] is the volume of carrier gas passing through the column over a period of t_r with carrier gas flow Fm [m/ min^{-1}]

$$V_r = F_m \cdot t_r \quad (16)$$

d_m - dead retention distance

t_{mm} - dead retention time

V_m - dead retention volume

And they are counted as retention parameters for other substances. One of the commonly used retained components in a gas chromatography is methane. Reduced retention parameters d_r, t_r, V_r are obtained as respective dead retention parameters, namely

$$D_m = d_r - d_m \quad (17)$$

$$t_{mm} = t_r - t_m \quad (18)$$

$$V_r = v_r - v_m \quad (19)$$

The effectiveness of the chromatographic column

The separation efficiency of the chromatographic column, the lower zone is separated substances during passage through the column and a peak in the chromatogram is narrower. A measurement of the effectiveness of the chromatographic column is the number of theoretical plates N_T

The number of theoretical plates N_T is usually calculated from the relationship

$$16\left(\frac{t_r}{w}\right)^2 = N_T \quad (20)$$

Where t_r [min] is the retention time, w[min] is the peak width.

If one knows the column length L [cm], he can compute the height equivalent to theoretical plate H [cm]

$$H = \frac{L}{N_T} \quad (21)$$

Qualitative Analysis

The basis for the identification of substances in the gas chromatographic analysis, a consensus of values d_r, t_r v_r or unknown substance and measured under exactly the same experimental conditions. Other parameters are used to identify characteristics which are less dependent on the experimental conditions. General value, characteristic for the substance and the stationary phase, suitable for identification of substances from chromatographic data, the retention index i.e. the relative retention characteristic relative to the scale of the retention characteristics of selected standards. As a standard substance for the determination of retention indices in gas chromatography n-alkanes are used, which are subject to the logarithms of the reduced retention time and are linearly dependent on the number of carbons in molecule. Identification of substances in the sample is done by comparing the calculated values with values of retention indices. The most reliable method of qualitative evaluation in gas chromatography is used as a mass spectrometer detector (MSD). This detector will provide the weight spectrum for each peak Fragment ions corresponding to the time-temperature disintegrating molecule weight and amount of ions are characteristic for a given substance. The obtained spectra are compared with spectra tabulated and the substance is in most cases unambiguously determined.

Quantitative analysis

The amount of substance separated leaving the column is measured by detectors. Automatic stage determines very rough estimate of the peak area number using database. It depends upon

-The effectiveness of the chromatographic column

-The separation efficiency of the chromatographic column, the small zone where substances are separated during passage through the column and a peak in the chromatogram is measure of the effectiveness of the chromatographic column in the number of theoretical plates N_T.

The number of theoretical plates N_T is usually calculated also from the relationship.

$$N_T = 5{,}54\left(\frac{t_r}{w^{1/2}}\right) \qquad (22)$$

t_r-retention time , $w^{1/2}$ peak width at half height.

In the case of narrow and symmetric peaks the relationship between the surface can be used for quantitative evaluation of the peak height. Height and peak concentrations (mass) components can be expressed usually by linear dependencies that apply generally in the range of several orders of concentrations of the substance for the quantitative determination, such as standard addition method, the method of internal standard.

Used detectors

ECD

Electron Capture Detector reacts with all electronegative elements such as (F, Cl,-OCH3,-NO3) and hydrocarbons for Selective Br, Cl, methoxy and nitrogroup. Environment vaporized substances and halogen substances with low content CL1, CL2
can not be detected properly.

PID

Photo ionization universal and selective detector depends on the energy supplied without gas, only for substances with low ionization potential of about 10 ev.

ELCD

Electrolytic conductive detector is used for capillary chromatography, for analysis of selective environment for halogen, amino, nitrogen, without radioactivity where only calibration is sufficient.

FPD flame

Photometrical mode detector is used for sulfur and some phosphorus detection as the FID used for phosphorus mode adds more flame gas for better resolution and selectivity.

FID flame

Ionization universal detector is very sensitive robust detector for fragrant, aromatic, compared to diesel and does not use gasoline or complex matrix component.

NPD

Nitrogen-phosphorus modified detector is used only for nitrogen and phosphorus. They are very sensitive and selective in the analysis of ECD detection or mass detection.

PDD impulse

Discharge universal detector is very non-radioactive sensitive, nondestructive detector used for the aliphatic components, petrochemical, refinery etc.

Tab.4 Types of detectors [22]

ECD	Reacts with all Electronegative elements such as (F,Cl,-OCH_3,-NO_3, and hydrocarbons	Typical detector of Environment vaporized Substances and halogens	Substances with low contentCl1,Cl2Can not be well detected
PID detector	Universal and selective	No gas, robust	Substance with low ionization potential of about 1 eV
ELCD detector	, for analysis in the environment	Only calibration is sufficient	
FPD detector	Mode for sulfur and phosphorus	For phosphorus vice flame mode	Add gas For better Resolution
FID detector	Very sensitive robust and detector	For diesel and gasoline	Do not use Analysis Complex Matrix component
NPD detector	modified FID detector	Very sensitive and selective	Add a mass detector
PDD detector	Universal, very sensitive	For petrochemical	As a FID detector

The output is then passed through the column to the detector, which converts part of the focus on the electric signal, the type of detector used with the GC depends on the application used in most of clinical laboratories, such as thermal conductivity detector (TCD), flame ionization detectors (FID), ECD, nitrogen phosphorus detector (NPD), and mass spectrometer detectors (MSD). GC can be used as detector for passage of a series of gases, provided that such process is not destructive, or that the sample-detector, which is destructive to the sample, is set as the last in the series. TCD determines changes in the thermal conductivity of the carrier gas caused by sample components. Gases like helium are used to increase sensitivity. FID used for easy ionization of organic samples such as amphetamines, barbiturates and steroids.FID is very sensitive to impurities in the past, detection systems often use one flame as a reference, measuring only carrier gas (basic), while the second measured sample, the difference between the two was intended as integrator, which informs about the current retention times, but is only one flame is needed for integrators used for the operation of two samples at a time. Other detectors use ionization, as ECD, and PID are-specific substances. ECD is used primarily to measure the halogenated gases such as chlorine and fluorine. Like FID which employs electrodes. Instead of detecting the current rise or fall, ECD detects the current produced by the interaction of the sample gas with electrons. ECD is the most sensitive and selective detector, but should only be used when the FID is insufficient because it requires a radioactive source ECD. NPD (also known as an alkaline flame ionization detector), are very similar FID except that the flames are sensitive to phosphorus or nitrogen containing compounds. They have a photon source specifically for the chemical structure, such as flavoring substances. MS can be connected to the GC detector location, even though the GC operates at pressure, while operating under high vacuum MS. GC with capillary columns reduces the pressure to a level easily handled with under-pressure MS, but when packed columns are used at a higher rate of gas flow, there are special separators needed to reduce the volume of gas in the MS. Waste gas leaves the column analysis, enters the ionization chamber where it is ionized by electron beam mass analyzer. Ions are separated according to their mass ratio, resulting in a characteristic spectrum that can be displayed on a CRT or printer, electrometer amplifies the signal. Detector helps to avoid congestion, and transmits it to the integrator that performs calculations and prints or displays the results. Problems are reported due to the rigidity and fragility of glass capillary columns to replace silica capillary columns. Impurities are not removed from the samples which contaminate the column, and cause unclear integrator among most other problems, such as poor sealing

injection port (cases due to water failure to replace the bulkhead in the required intervals), column contamination in the detector and the rest are caused by improper maintenance of the unit. Mandatory rating indicates that this specification is the minimum necessary for the system to perform its functions. It is used for specifications that will enhance either test parameters or ease of use, and therefore efficiency. Rating indicates optional specification that does not affect how the system performs its function, but the presence of these options will allow wider use of applications by offering more options testing or minimizing interaction with the user, which allows the system to effectively operate in different circumstances. Many features of gas chromatography will be based on the needs of a particular device. However, certain minimum requirements are common to most applications. For example, the system includes capillary chromatography columns; other columns may be based on the intended use of the device. There must be at least one detector, but the detector may be more desirable for certain applications more detectors should be avoided, if there is a risk of damage to the specimen. Some of the data management functions should be available with chromatography system necessary to produce test results. Data interpretation software is required to present the results in useful format without manual interpretation given GC with ECD a radioactive source. The most common detectors used in gas chromatography is a flame ionization detector (FID). It is a detector capable of detecting nearly all organic substances with a wide range of concentrations. Its principle consists in measuring the change in electrical conductivity of the hydrogen flame caused by the presence of organic matter. The detector consists of pilot burner, inlet at the bottom of the carrier gas exiting the column, additional inert gas (nitrogen) and hydrogen. [18].

GC

Saturn 2000 GC / MS mass spectrometer Saturn GC / MS uses ultra trace ion trap mass spectrometer. Gas chromatographs (GCS) analyze volatile samples separated into their components, which are identified on the basis of measuring their retention time in the column (the time required from sample injection on the peak specific folder with similar vapor pressures and chemical structures.

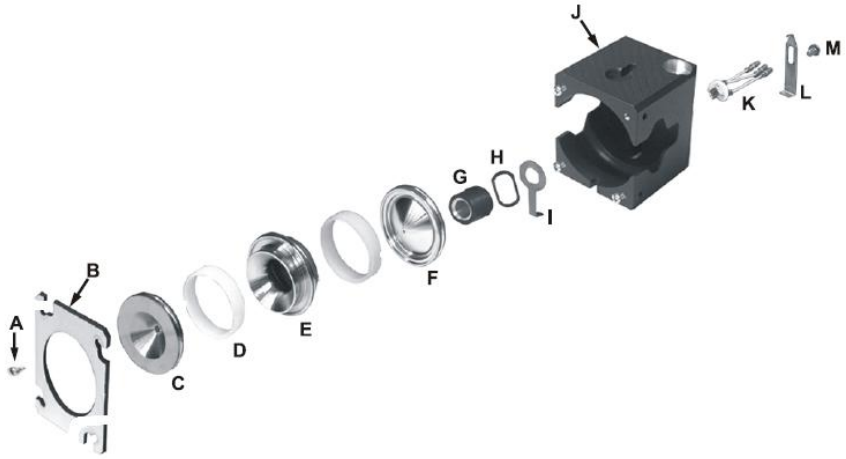


Fig.12 Ion Trap [20]

A	Screw 6/32	H	Washer
B	Mounting plate	I	Input conductor
C	End electrodes	J	Furnace
D	Quartz or silica	K	Filament Assembly
E	RF electrodes Ring	L	Filament
F	End Cap Screw electrodes	M	Screw
G	Electron Gateway [20]		

Ion trap

Trap furnace generates heat for thermal control; it is unlikely that two fibers will have the same net inflow of electrons in the ion trap, so that the amplitude of the signal from two different fibers was the same.

Electron gate

Electron gate is a cylindrical electrode that controls the entry of electrons into the ion trap and its ion trap group has three stainless steel electrodes.

Electron multiplier

Electron multiplier is fixed in a preset position on the protective metal clip that can be easily removed and replaced.

Stable reading

Fore line pump has two purposes. The pump is connected to the rear panel socket marked voltage - pump on the back of power supply side is outlet, which is controlled by a switch.

Rear panel

Fore line pump used on the Saturn GC / MS is a two-stage rotary pump with a pumping speed of 90 ml/min and vacuum potential of 1.5 x 10^{-2} torr (2 x10^{-2} torr). RF generator assembly consists of a plate circuit detector link and shielded with coils under vacuum manifold housing, which surrounds the detector coil and the circuits. [20]

Hard ionization technique is used in the gaseous phase. The most common and most advanced ionization method is well reproducible spectra production process. The interaction of the material with shock-accelerated electrons in high vacuum is preferred. Ionization of the source, transfer of substances to ionized state, the destruction of chemical bonds primarily resulting in ion formation and fragments. Analysis after separation in ion analyzer (separator) is distributed in space or time. A mixture of ions is produced in the ion source.

Detection

The detection is made from a direct stream of separate ions which is a signal proportional to the number of ions. It is transferred to a computer and processed using the software in the form of weight spectra.

Registration and inspection

Also, the computer registers the analytical data, manages and controls the operating conditions of the apparatus. Ionization is done in mass spectrum. Ionization of substances is essential for analysis as the information obtained applies only to charged particles or ion. Energy necessary for ionization depends on the substances.

Soft ionization

The excess energy supplied ionizes molecule to small particles and fragmentation is low such as chemical ionization (CI)

Hard ionization

The supplied energy leads to extensive fragmentation primarily forming ions such as electron impact ionization, electron impact (EI).and For TOF(time of flight):

$$\frac{m}{z} = 2eEs\left(\frac{t}{d}\right) \tag{23}$$

For analysis of TOF (time of flight) the parameters are

$\frac{m}{z}$ - mass to charge ratio

e- elementary charge

E- pulse potential extraction

s- length acceleration

t- time of flight

d- length of flight

Chemical ionization

The soft ionization technique of vapor uses low fragmentation energy source, although with rapid flow of electrons the energy is transmitted through a chemical medium, which is introduced into the ionization chamber, thereby increasing the possibility of intra and intermolecular interactions and recombination under elevated pressure. Reaction medium may be methane, isobutane, methanol vapor, acetonitrile, etc. When there is a transfer of a proton from the cation exchange reaction gas at a neutral molecule, the resulting spectra are difficult to standardize and depends on the working conditions in the ion source. Complement equipment along side is important for determining the molecular weight. In case of negative chemical ionization, there is occurrence of negative ions much lower than positive. In the lower weights the ions do not have structural significance. However, the reaction medium is reluctantly proton donor (AFIN large proton-one), which causes the formation of anions (eg, dichloromethane, ammonia), which generate negative ion clusters with substances of high electron affinity causing a consequent significant increase in sensitivity. [20]

3.15 Biotechnology cotton

Genetics in 21st Century can safely be described as one of the scientific disciplines that trends other biological research. Genetics from the last century can be just downstream research in biochemistry, clarification of molecular principles of heredity and variability of living organisms. Discovery of the structure of nucleic acids and genetic mechanisms influence research regulations in genetic activity, which laid the foundation for self-disciplined molecular biology. Linking modern scientific disciplines with progressively developing new technological fields, allows quick transformation of the latest developments in genetics and applied sphere. The use of GM plants for breeding new varieties made additional contributions, which are focused on practical application and evaluation of GM plants in terms of their use and ecological risks of growing. GM cotton has become widespread, covering a total of 15 million hectares in 2007, or 43 percent of the world's cotton. Most GM cotton is grown in India and the US, but it can also be found in China, Argentina, South Africa, Australia, Mexico, and Columbia. More than half (68%) of China's cotton production is genetically modified to produce a substance B_t that protects it against insect and pests. Cotton used to be protected from insects by repeated pesticide applications. Bt cotton has now enabled Chinese farmers to dramatically reduce pesticide use. The production of GM cotton has not yet been approved in the EU. Applications have been submitted, but a decision is still pending. Several lines of GM cotton have been approved in the EU, but only for use as food and feed. A brief account of the practical use of plant varieties resulting from genetic modifications is as follows:

- High resistance or tolerance to herbicides
- Resistance to insect pests
- Resistance to viral, bacterial and fungal diseases

-Tolerance to herbicides

-Increased durability of products

-Induction of male sterility

-Production of specific proteins including vaccines produced by the plant

-Production of vegetable oils with modification

-Production of specific carbohydrates.[25]

3.16 Detection of genetically modified cotton

Problem of declaration as biotechnology cotton which does not respect the standards is a serious problem. Demand for biotechnology cotton is growing and estimated at 40% for all cotton market. The biggest problem is now, how to define standards for genetically modified cotton, according to the 2092 / 91EU. Other states have their own legislation and standard for harvesting and the use.In 2007, there were 20 types of GM cotton grown on 15 million hectares, around 66% of Indian, 68% Chinese, and 90% of GM cotton from USA.

Properties of GM cotton are:

-Tolerance to herbicides

-Produces its own insecticide

-Resistance to pesticides

-Adapts well to both large and small variations in salinity and humidity

-Sufficient strength and sufficient maturity

Nowadays certification is made on the basis of documents that are really inadequate. This is the reason why genetic detection system module was developed which is based on analysis of DNA deoxyribonucleic acid. All organisms are based on the DNA-based block that is repeated nucleotide/adenine, thymine, cytosine, guanine and these blocks are different for each organism. The process of analysis has three stages:

-DNA extraction (Major problem in the extraction of existing DNA is that it is not clean enough and the quality of the DNA is not detected)

-Polymerase PCR / polymerase chain reaction (It runs on the enzymatic method, which is generated by millions of similar molecules. Typical polymerase chain reaction consists of 35 to 50 cycles and each cycle has three stages.)Denaturation of the components required for the synthesis of double bottoms Based on the discrete information followed by classification, all this information could be obtained on the international data base. For this phase is a common summary, the individual denaturation and annealing shows existence of new DNA.PCR (polymerase chain reaction)electrophoresis will detect agarose-gel. Genetically modified plant genes contain new plants and it gives new features such as herbicide tolerance and resistance to the insecticides. Genes function depends on the controllers which determine which base is known as promoter or terminator. Most of the plants contain these ingredients and the best known are 35s CAMV promoter, Cauliflower Mosaic virus, the trailing

characters from some genes as ago bacterium tumefactions. One gene or genes which are much interconnected with corresponding controllers is called structural gene; this indicates the presence of GM in the plant but does not specify the type of GM plant .Objective of this analysis is to look for presence of a DNA sequence and by comparing the original and structural gene, the type of the gene can be assessed and accurately identified.[30]

4. Experimental part

For experiments the following organic and conventional cottons were used

Tab.5 Samples used for analysis

Reference cotton	**Name**	**Origin**
Con-1	Conventional cotton year 2007	Senegal
Con-2	Conventional cotton year 2008	Senegal
Bio-1	Organic cotton year 2007	Senegal
Bio-2	Organic cotton year2008	Senegal
a-1	Conventional Cotton Giza45-yoroc F6 AI/38 KTM TUL	Egypt
b-1	Conventional cotton AI/69 KTM TUL	Russia
c-1	Conventional cotton T427, MVLSP AI/80 KTM TUL	Indie

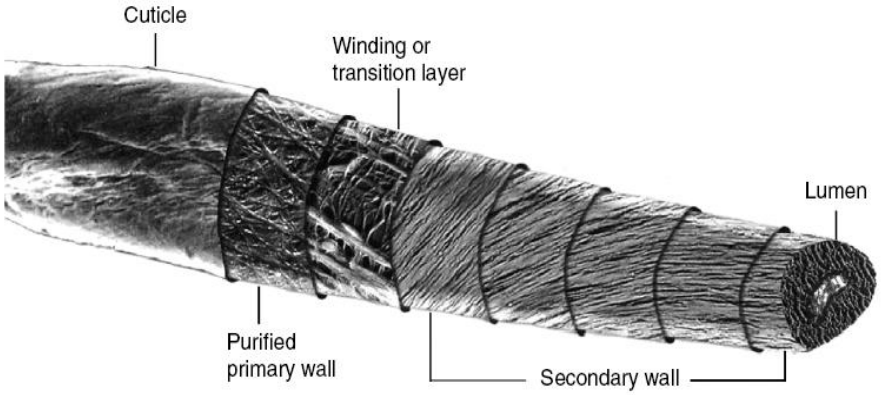


Fig.13 Structure cotton TEM / SEM [7]

A computer generated montage of a fiber segment is constructed from individual transmission electron micrographs (TEM) and scanning electron micrographs (SEMs) of layers of the fiber to show an overview of the layered structures of the fiber. Fiber surface, primary wall, and secondary layers have been shown at different magnifications to better visualize fibrillar structures and the various fiber layers from surface to lumen. The surface marked cuticle is an SEM view of a scoured and bleached fiber surface and was used as the skeleton of the montage. All other segments are taken from transmission micrographs and are shown at higher magnifications. No fibrils are visible in the SEM of the cuticle because of its relatively low magnification as well as the presence of noncellulosic materials. The fiber surface at the cut end of the fiber shows fibrils that have been separated by swelling. Although the montage uses actual pictures of cotton fiber layer structures, it is intended to represent possible fiber morphology rather than to indicate an exact cotton fiber structure. (Credit to Wilton Goynes.) [7]

4.1 Geometrical properties of organic and conventional cotton

4.1.1 Length with staple diagram

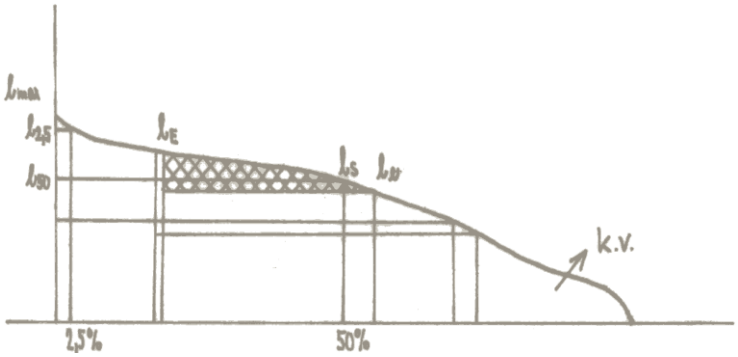


Fig. 14 Organic cotton by staple diagram bio-2

On axis x H(I) –Probability occurrence of fiber length longer than l

On axis y Length l

lmax =32 mm

lE large effective length =25mm

le small effective length =19mm

Ls mean length =23 mm

The uniformity of =75.41%

Dispersion = 24%

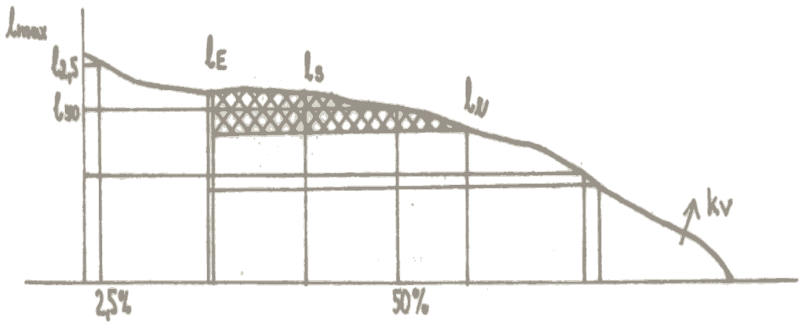


Fig. 15 Conventional cotton of staple diagram con-1

On axis x H(I) –Probability occurrence of fiber length longer than l

On axis y Length l

lmax =33 mm

lE large effective length =25mm

le small effective length of =20 mm

Ls mean length =27 mm

Dispersion =20%

The uniformity of =79.37%

4.1.2 Maturity with polarized lighted microscope according to standard CSN 80 0311

Calculation of maturity

-For conventional cotton con-1

Total	299
Mature	172
Medium mature	125
Dead	2

$$N_m = \frac{(172 \cdot 3.0) + (125 \cdot 1.5) + (2 \cdot 0.5)}{299} = 2.35 \qquad (24)$$

Conventional cotton con-1

class 4

-For organic cotton bio-2

Total:	295
Mature:	148
medium mature:	141
Dead:	6

$$N_m = \frac{(148 \cdot 3.0) + (141 \cdot 1.5) + (6 \cdot 0.5)}{299} = 2.23 \qquad (25)$$

organic cotton bio-2

class 4

4.1.3 Fineness of organic and conventional cotton with micronaire

Table. 6 Calculation of the fineness of organic and conventional cotton

	conventional cotton con-1		**Organiccotton bio-2**	
	MIC	dtex	MIC	dtex
	4,80	1,89	4,35	1,71
	4,80	1,89	4,30	1,69
	4,90	1,93	4,65	1,83
	4,70	1,85	4,45	1,75
	4,85	1,91	4,60	1,81
	4,75	1,87	4,40	1,73
	4,80	1,89	4,30	1,69
	4,70	1,85	4,30	1,69
	4,80	1,89	4,40	1,73
	4,75	1,87	4,35	1,71
	4,65	1,83	4,40	1,73
	4,75	1,87	4,50	1,77
	4,85	1,91	4,30	1,69
	4,70	1,85	4,25	1,67
	4,80	1,89	4,35	1,71
average	4,77333333	1,879333	4,393333	1,727333
standard dev.	0,06548961	0,026196	0,110855	0,044342

Table.7 Fineness standard according to CSN 800311

MIC	T[dtex]	
3	1,18	Very fine cotton
3-3,9	1,18-1,54	Fine cotton
4-4,9	1,58-1,94	Medium fine cotton
4,9-5,9	1,93-2,32	Medium coarse cotton
Nad 6	Nad 2,364	Coarse cotton

4.2 Mechanical properties of organic and conventional cotton

Mechanical properties of cotton fibers are very important in order to assess useful properties of fibers like strength, elongation.

4.2.1 With vibroscope and vibrodyn 400

Fineness and Strength of individual cotton fiber is estimated.

Tab. 8 Statistics of mechanical properties of conventional and organic cotton

Organic cotton bio-2	F_{max} [N]	E [MPa]	A_{max} [%]
average value	0,0422	1,654	5,13
standard deviation	0,01755	0,7171	2,06

conventional cotton con-1	F_{max} [N]	E [MPa]	A_{max} [%]
Average value	0,0448	1,3598	5,81
standard deviation	0,01496	0,5505	2.22

Tab. 9 Result of relative strength of organic cotton by Pressley Tester

Conventional cotton con-1				
N	F [lb]	m [mg]	F [N]	Fr [N/dtex]
1.	15,6	4,94	7,07	7,67
2.	14,1	4,11	6,39	8,33
3.	13,5	4,97	6,12	6,6
4.	14,8	3,93	6,7	9,14
5.	13,4	4,42	6,07	7,36
6.	12,4	4,16	5,62	7,24
Average value	13,96666667	4,42167	6,32833	7,72333
Standard deviation	1,030641656	0,403461	0,466169	0,817041

Organic cotton bio-2				
N	F [lb]	m [mg]	F [N]	Fr[N /dtex]
1.	12,7	3,76	5,75	8,2
2.	12,2	4,55	5,52	6,5
3.	12,4	3,84	5,62	7,84
4.	14,4	4,88	6,52	7,7
5.	12,6	4,62	5,7	6,62
6.	12,2	3,57	5,53	6,62
Average value	12,75	4,20333	5,77333	7,24667
Standard deviation	0,76103	0,496879	0,344077	0,684268

4.2.3 Dynamic mechanical analysis (DMA)

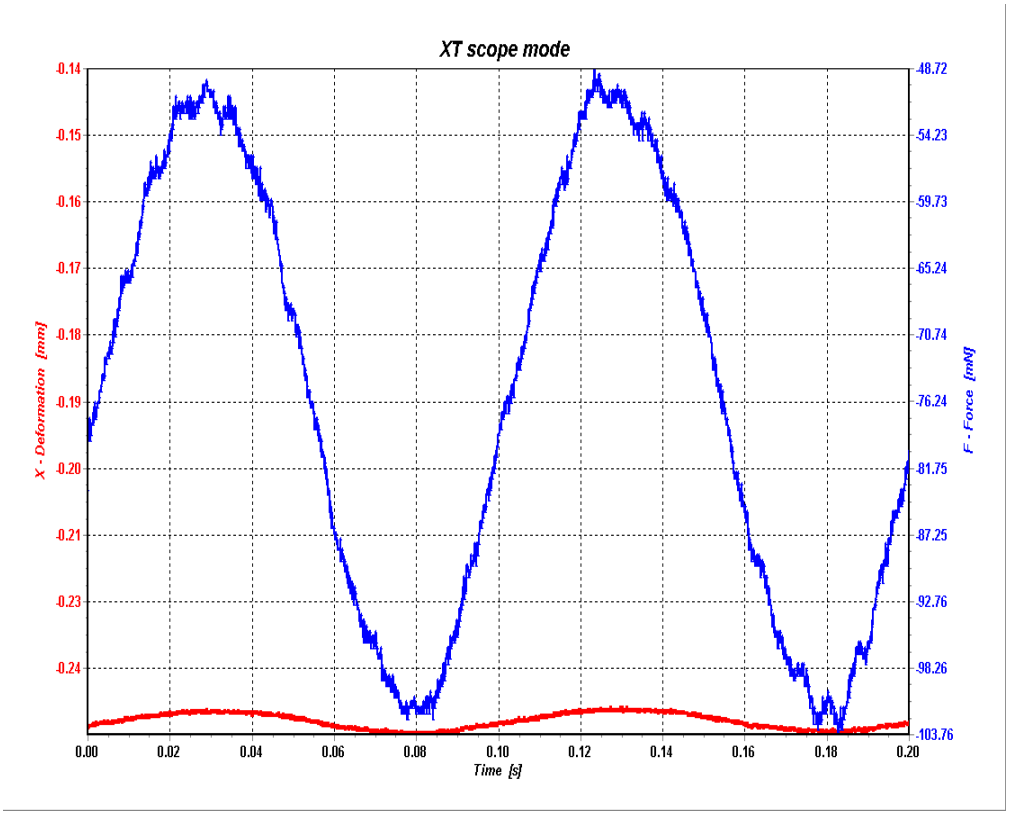


Fig. 20 Deformation and force dependence to time of conventional cotton **Con**-1

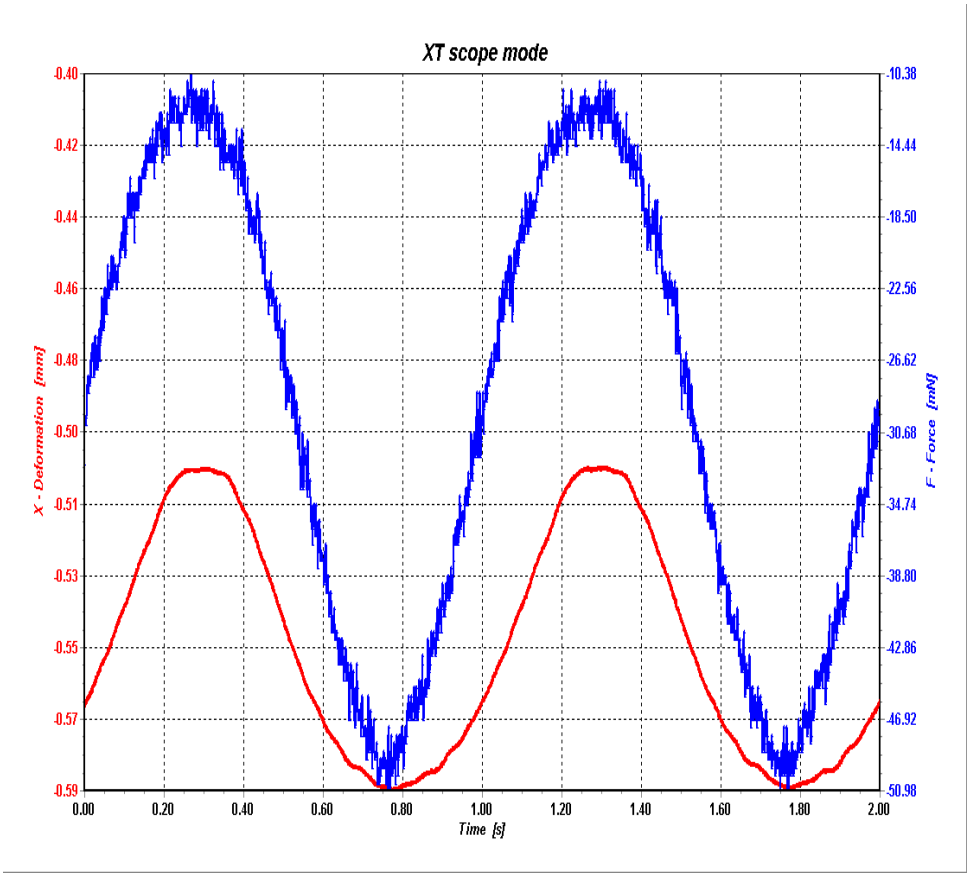
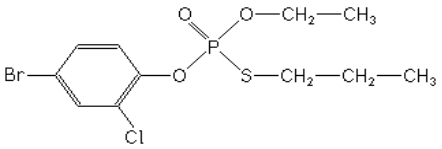
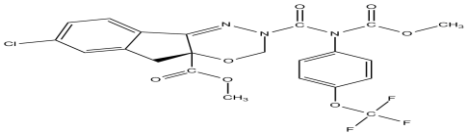
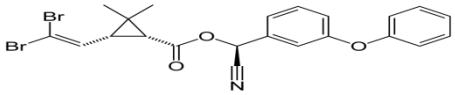
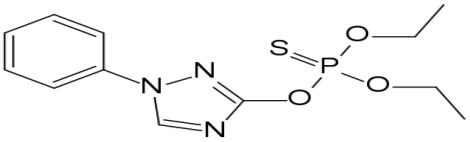
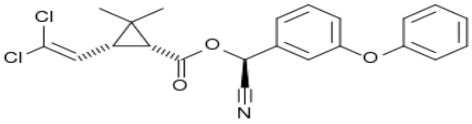
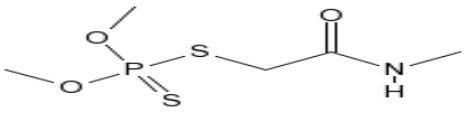


Fig. 21 Deformation and force dependence to time of organic cotton bio-2

4.3 Physical chemical analysis of organic and conventional cotton

Tab 10 List of pesticides from Senegal[3]

Profenofos	C11H15BrClO3PS 
Indoxacarbe	C22H17ClFN3O 
Deltamethrin	C22H19Br2NO3 
Triazophos	C12H16N3O3PS 
Cypermethrin	C22H19Cl2NO3 
Dimethoate	C5H12NO3PS2 

4.3.1 The results of gas chromatography with mass spectrum Varian 3800/2000

Princip of method

Silica column (fused Silicium)

Measurement parameters

Temperature 80 ° C-180 ° C

25 ° C / min. Up to a temperature of 300 ° C

Gas: Helium 1.3 ml / min.

Split injector less than 2.0 ml, temperature 250 ° C

Ionisation EI (electron ionisation)

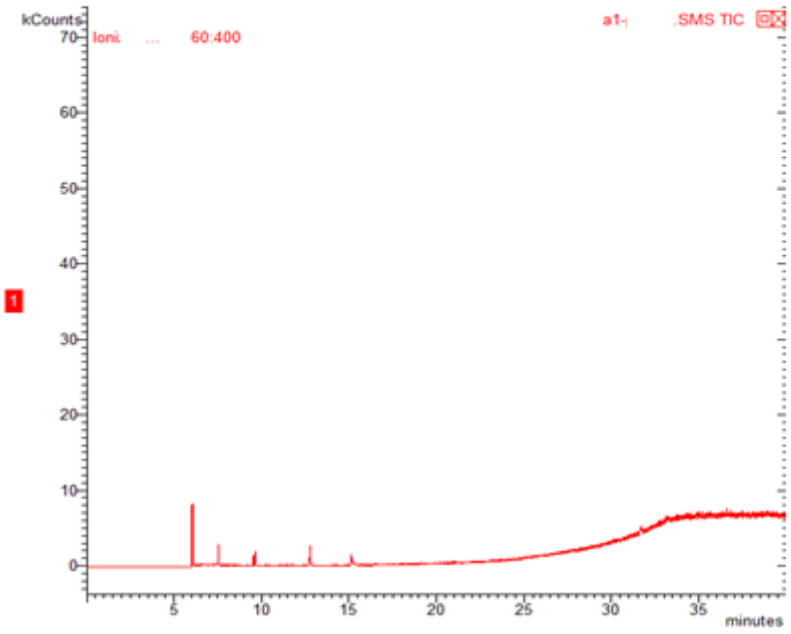
Dose per 1 ml of sample, solvent for rinsing 2 ml heptane.

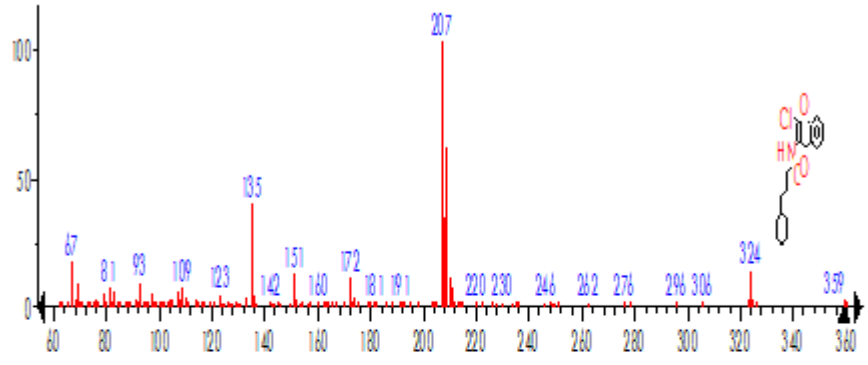
Based on samples of cotton available - cotton con - 1 of the 2007 harvest and cotton con-2 from the 2008 harvest, the cotton from Russia, China and Egypt, pesticide traces in the extract were observed.

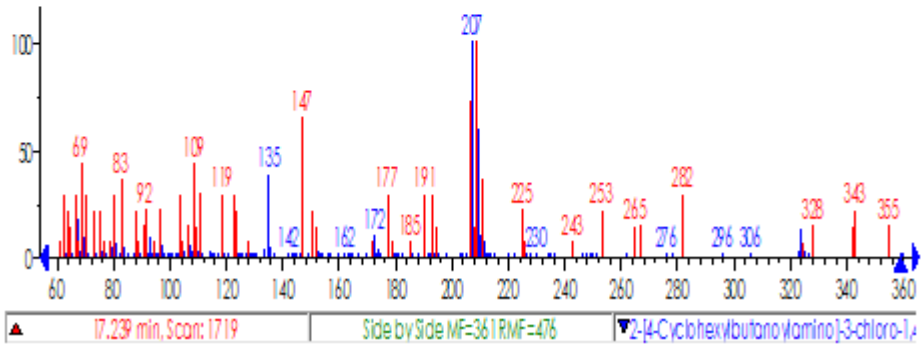
Preparation of extract

Sample of 1 g of cotton was extracted with 30 ml of dichloromethane (CH2Cl2) for 5 minutes to dissolve all anticipated substance in cotton sample. Using pesticides mix -10 (150 pesticides summary) the standard GC-MS or standard curve was determined with pesticide mix-10, but if the pesticides are not in the selected range (mix-10), they cannot be identified. The concentration of the extract was 0.03 g/ ml to 0.12 g / ml. Thus the occurrence of pesticides was observed on all cotton samples investigated. The analysis was done for the conventional cotton, organic cotton, conventional cotton with pesticide, organic with pesticide, a1-cotton from Egypt, b-1 from Russia and cotton c-1 of China. These extracts were monitored by GC-MS. The samples of organic cotton and conventional cotton were added with 1 ml mix-10.

Name: 17.239 min, Scan: 1719
MW: N/A ID#: 24 DB: Text file
Comment: ol SMS
10 largest peaks:
209.999 | 207.713 | 147.642 | 109.428 | 69.428 |
211.356 | 83.356 | 104.285 | 111.285 | 119.285 |
Synonyms:

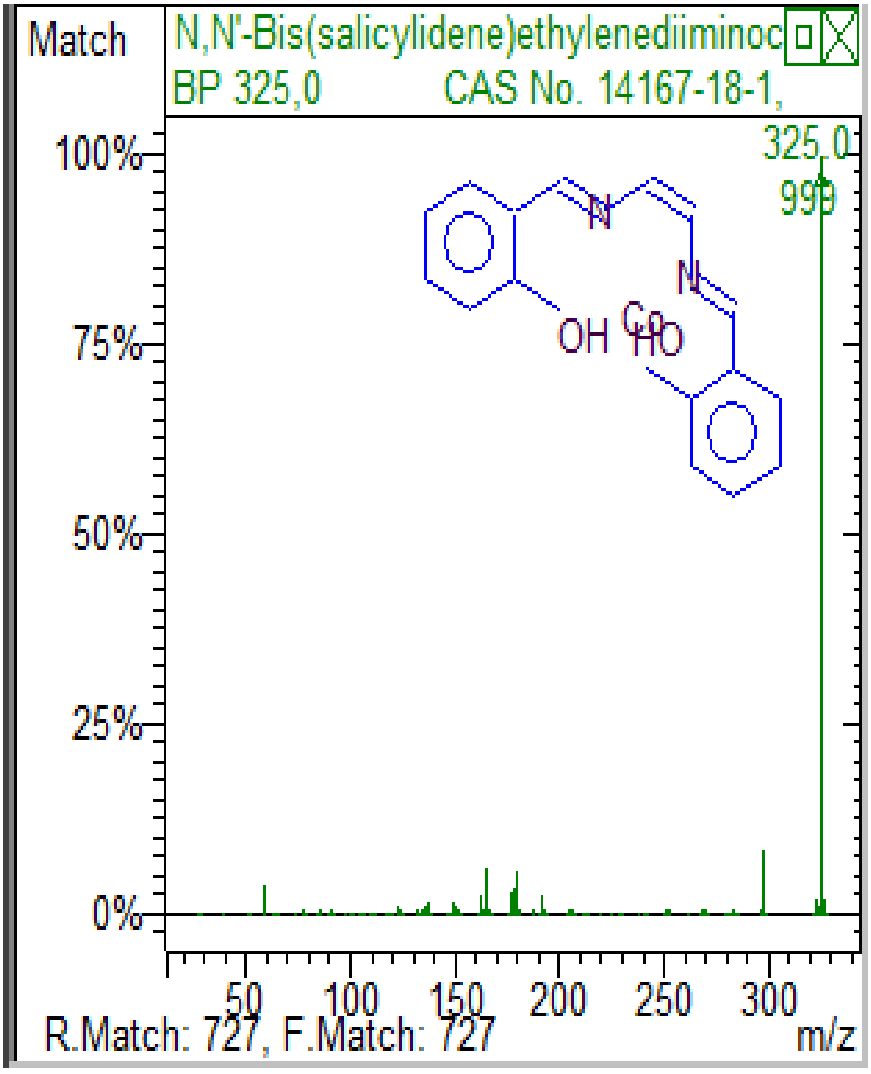






On axis x m/z (mass to charge)

On y abundance ratio



Figs.22 results from pesticides on cotton a-1 from Egypt from library

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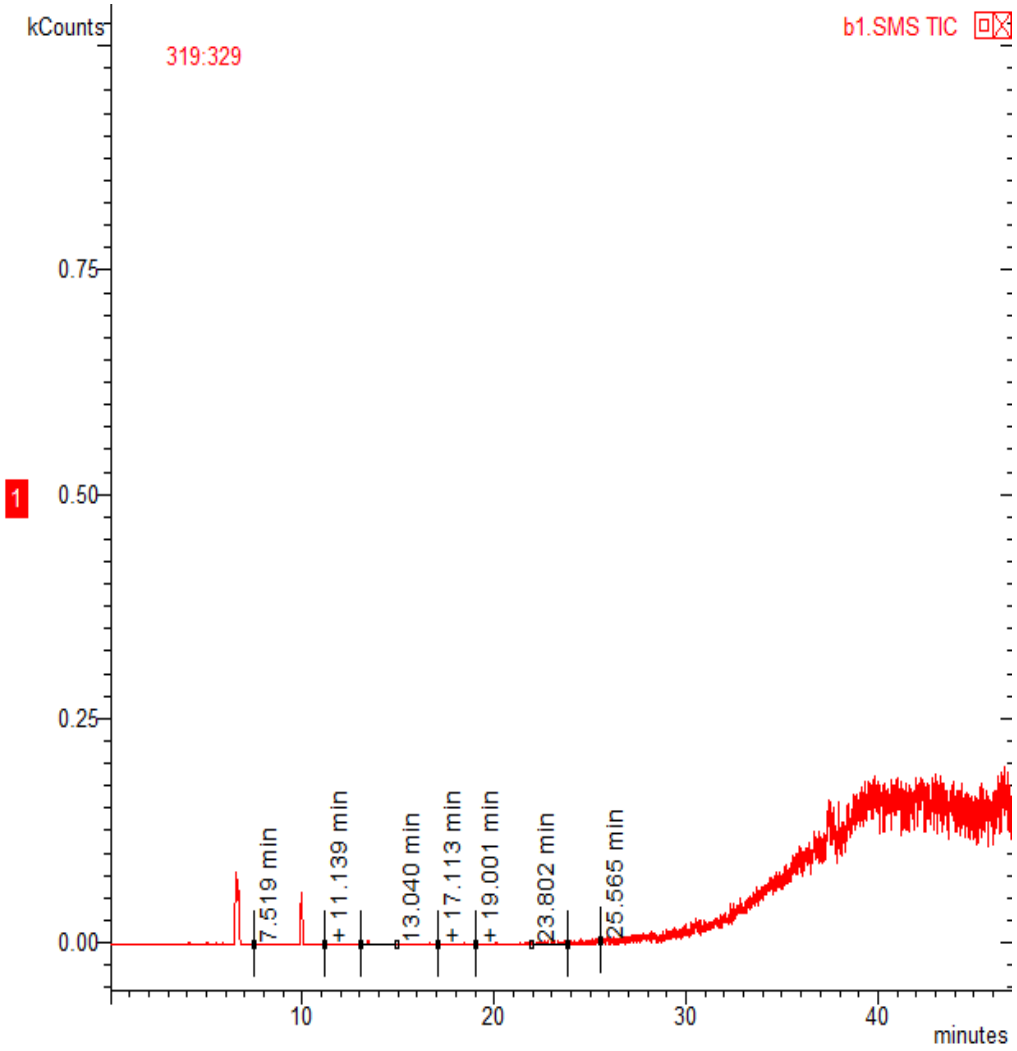
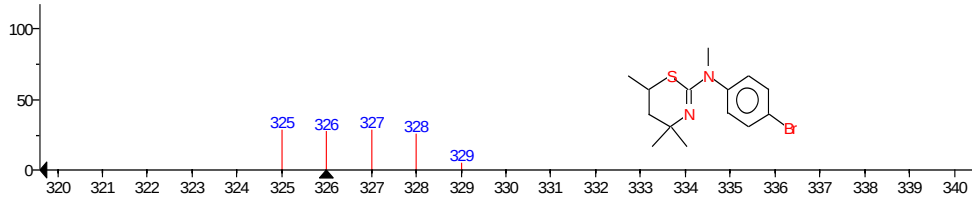


Fig. 23 Results of pesticides test on cotton b-1 from Russia

On axis x time

On axis y intensity signal (kcount)

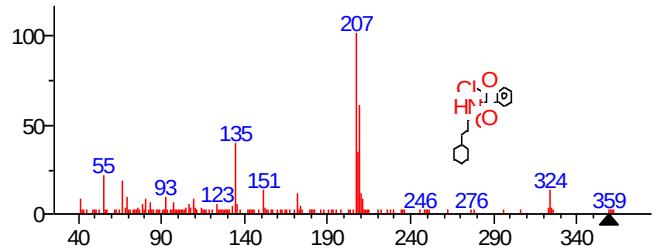
Name: 33.634 min, Scan: 3740
MW: N/A ID#: 29 DB: Text File
Comment: c1.SMS
4 largest peaks:
325 999 | 327 999 | 328 999 | 326 499 |
Synonyms:
no synonyms.



(mainlib) 4,4,6-Trimethyl-2-(N-methyl-p-bromophenylamino)-5,6-dihydro-4H-1,3-thiazine

Name: 2-[4-Cyclohexylbutanoylamino]-3-chloro-1,4-naphthoquinone
Formula: $C_{20}H_{22}ClNO_3$
MW: 359 CAS#: 25304-04-5 NIST#: 253796 ID#: 126797 DB: mainlib
Other DBs: None
Contributor: Div. of Experiment Therapeutics WRAIR, WRAMC, Washington DC 20307
10 largest peaks:
207 999 | 209 592 | 135 383 | 208 331 | 55 206 |
67 171 | 324 128 | 151 127 | 210 103 | 172 103 |
Synonyms:
1.N-(3-Chloro-1,4-dioxo-1,4-dihydro-2-naphthalenyl)-4-cyclohexylbutanamide #

Estimated Kovats RI:
Value: 3105 iu
Confidence interval (Diverse functional groups): 89(50%) 382(95%) iu



(mainlib) 2-[4-Cyclohexylbutanoylamino]-3-chloro-1,4-naphthoquin

Name: N-(2-Chloro-5-nitrobenzylidene)-N'-phthalazin-1-ylhydrazine
Formula: $C_{15}H_{10}ClN_5O_2$
MW: 327 NIST#: 284129 ID#: 109054 DB: mainlib
Contributor: A.Pleshkova, Nesmeyanov Inst.Org.Elem.Cpds, Moscow
10 largest peaks:
171 999 | 103 298 | 327 131 | 172 127 | 89 122 |
325 107 | 76 94 | 129 84 | 290 81 | 75 77 |
Synonyms:
no synonyms.

Estimated Kovats RI:
Value: 2995 iu
Confidence interval (Diverse functional groups): 89(50%) 382(95%) iu

On axis x m/z(mass to charge)

On y abundance ratio

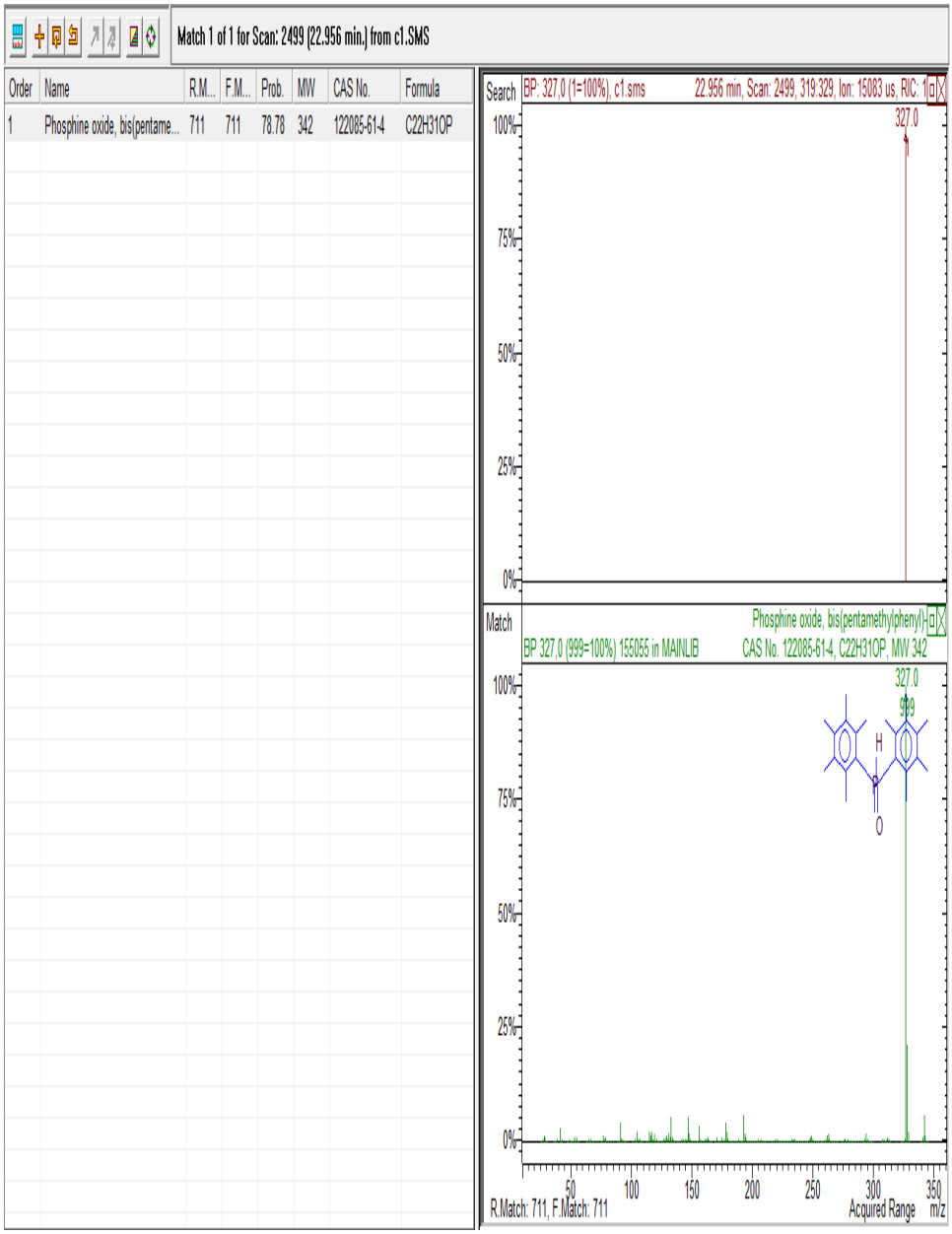


Fig. 24 Results of pesticides on cotton c- 1 from Indie from library

Sample from Indie on left and the chemical formula of pesticide on right are well known pesticides in cotton cultivation, those sample of cotton are 10 years old in the laboratory of textile engineering.

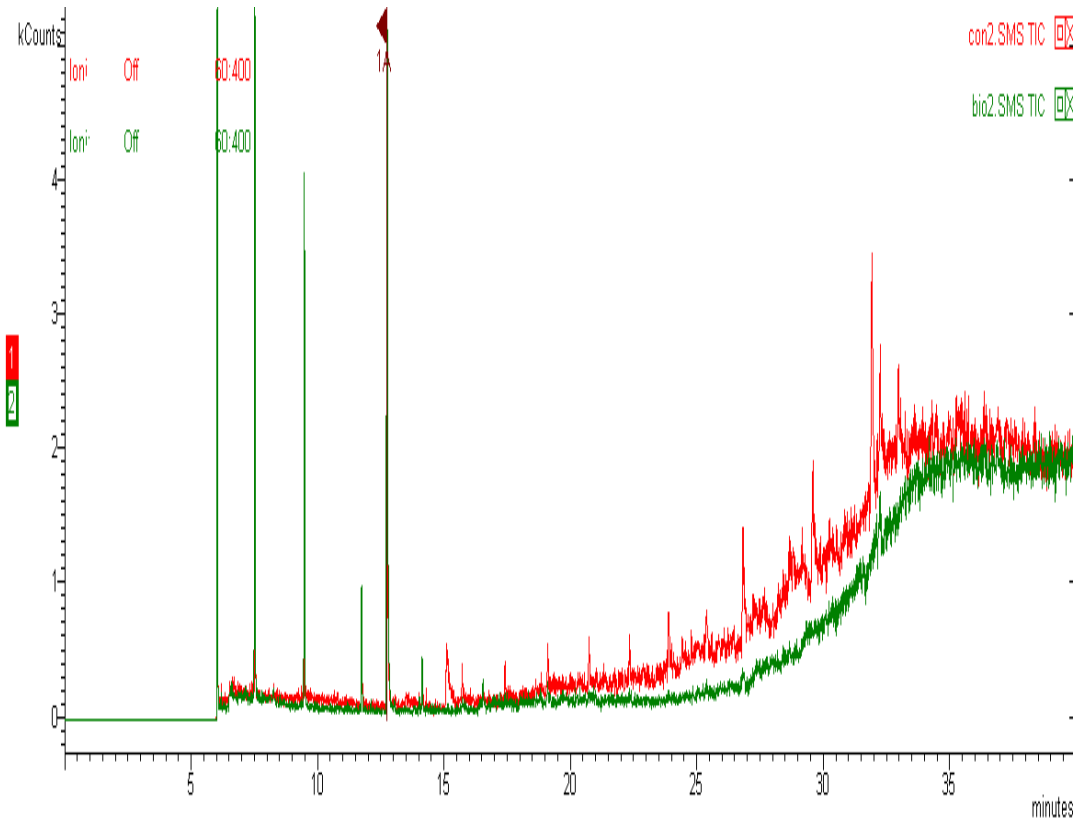


Fig. 24 Comparison of measured results of gas chromatography
Samples of organic and conventional cotton in 2008

The red one is conventional cotton con-2 and the green one organic cotton bio-2

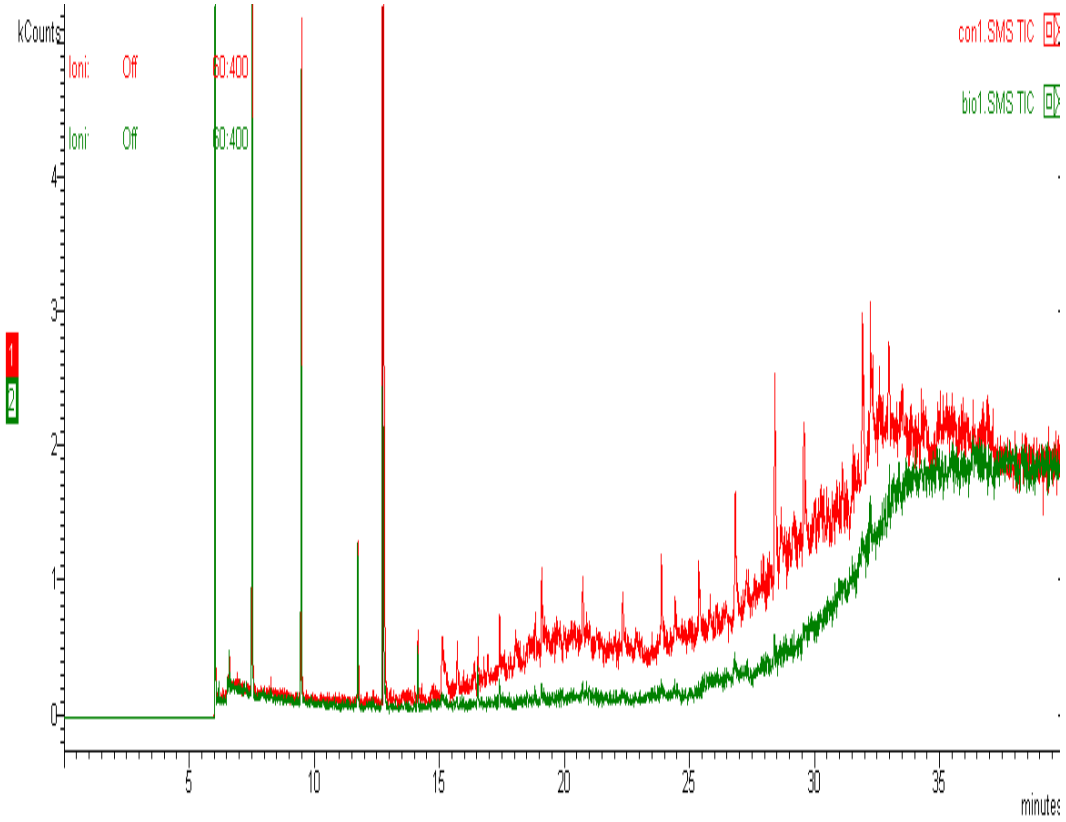


Fig. 25 Samples of organic bio-1and conventional con-1cotton from year 2007 1g/30ml

On axis x time

On axis y intensity signal (k count)

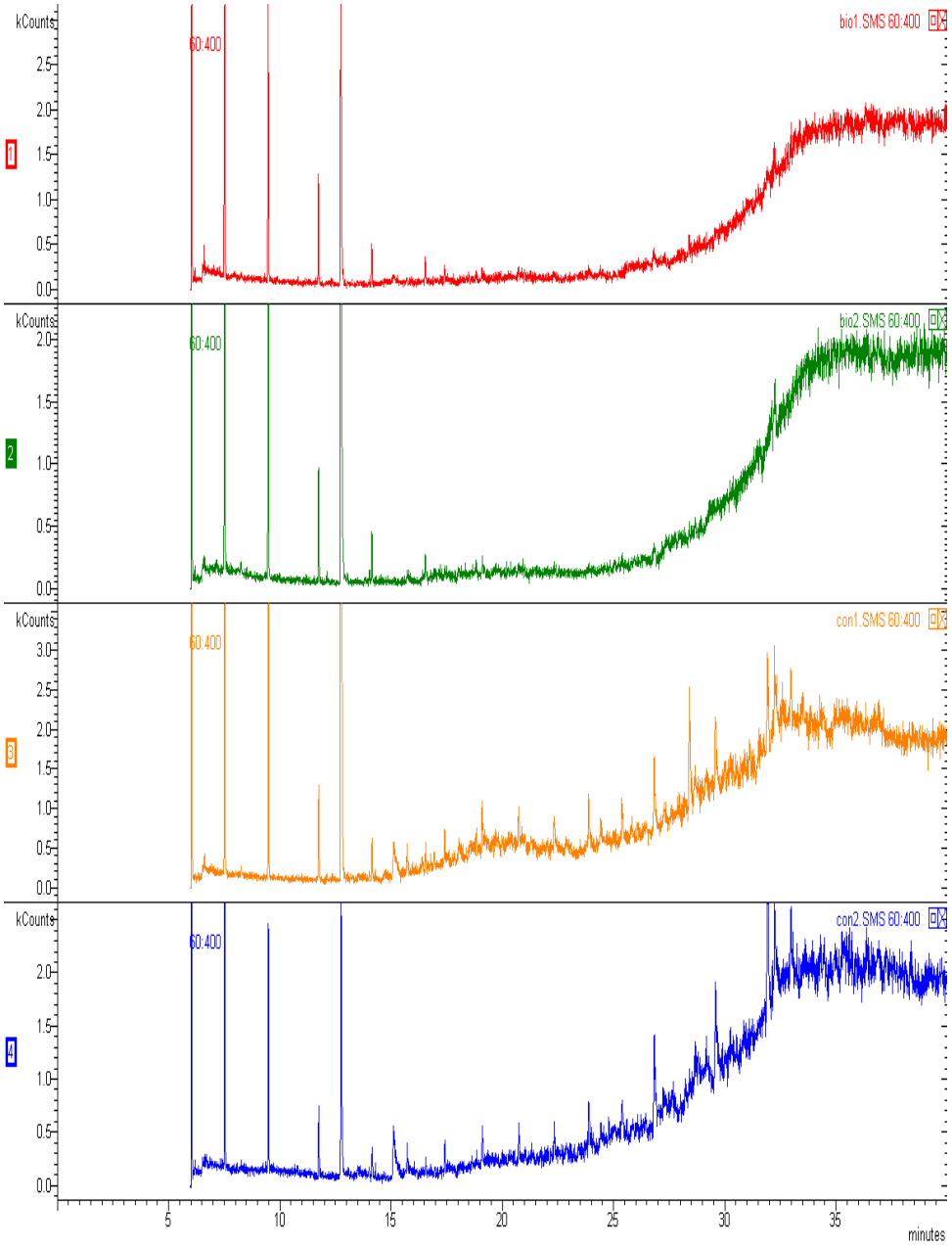


Fig. 26 Curve for organic and conventional cotton from year 2007 and 2008

The first two are organic and last two are conventional cotton

On axis x time

On axis y intensity signal (k count)

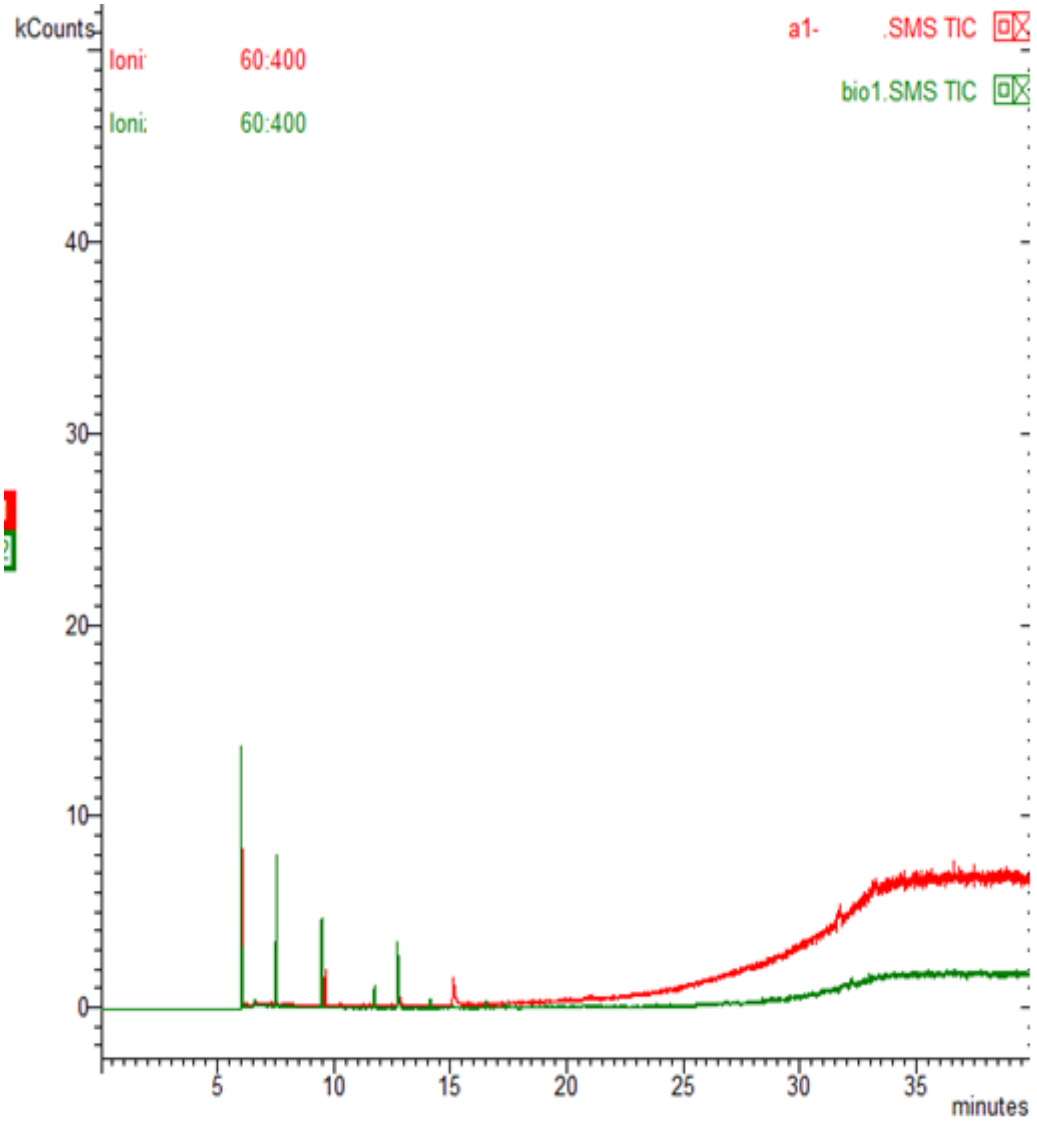


Fig. 25 Comparaison curve a-1 sample from Egypt and bio-1 organic cotton from Senegal

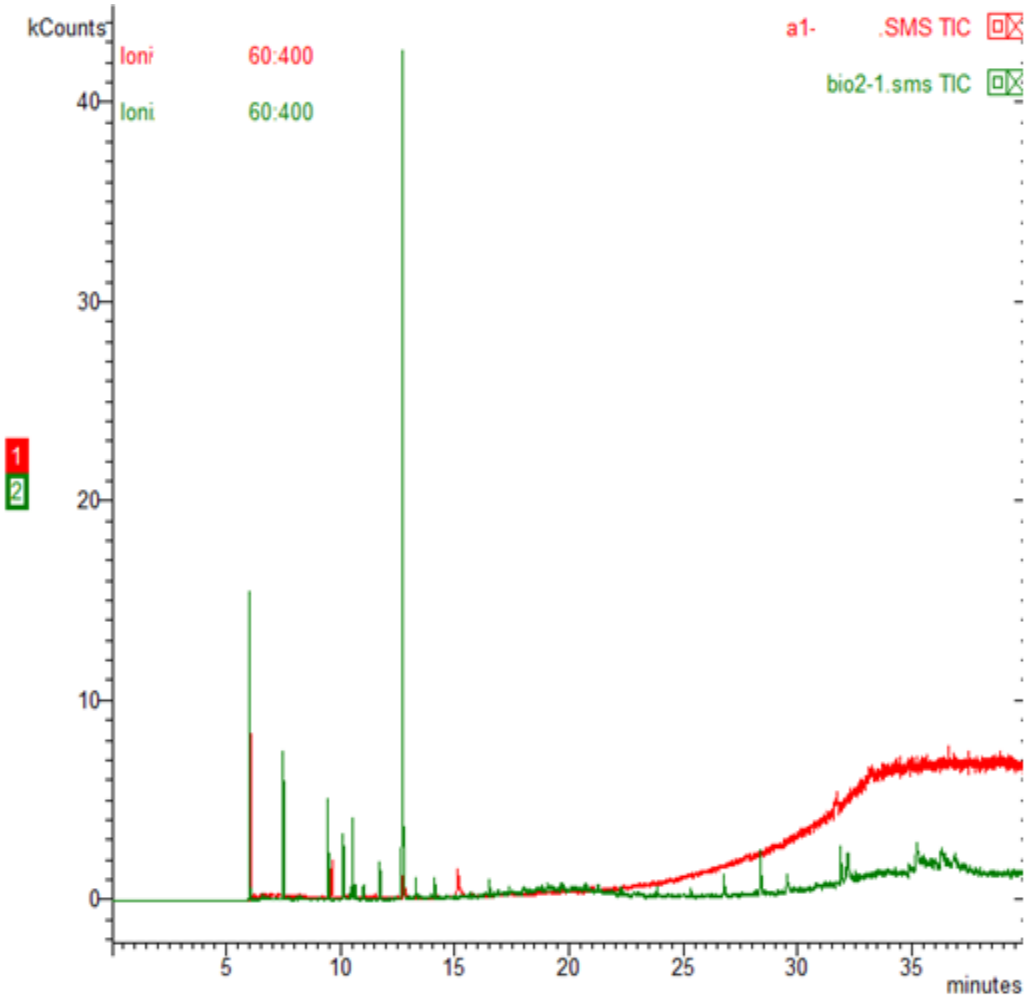


Fig. 26 Cotton a-1 from Egypt and organic cotton bio-2 from Senegal

On axis x time

On axis y intensity signal (k count)

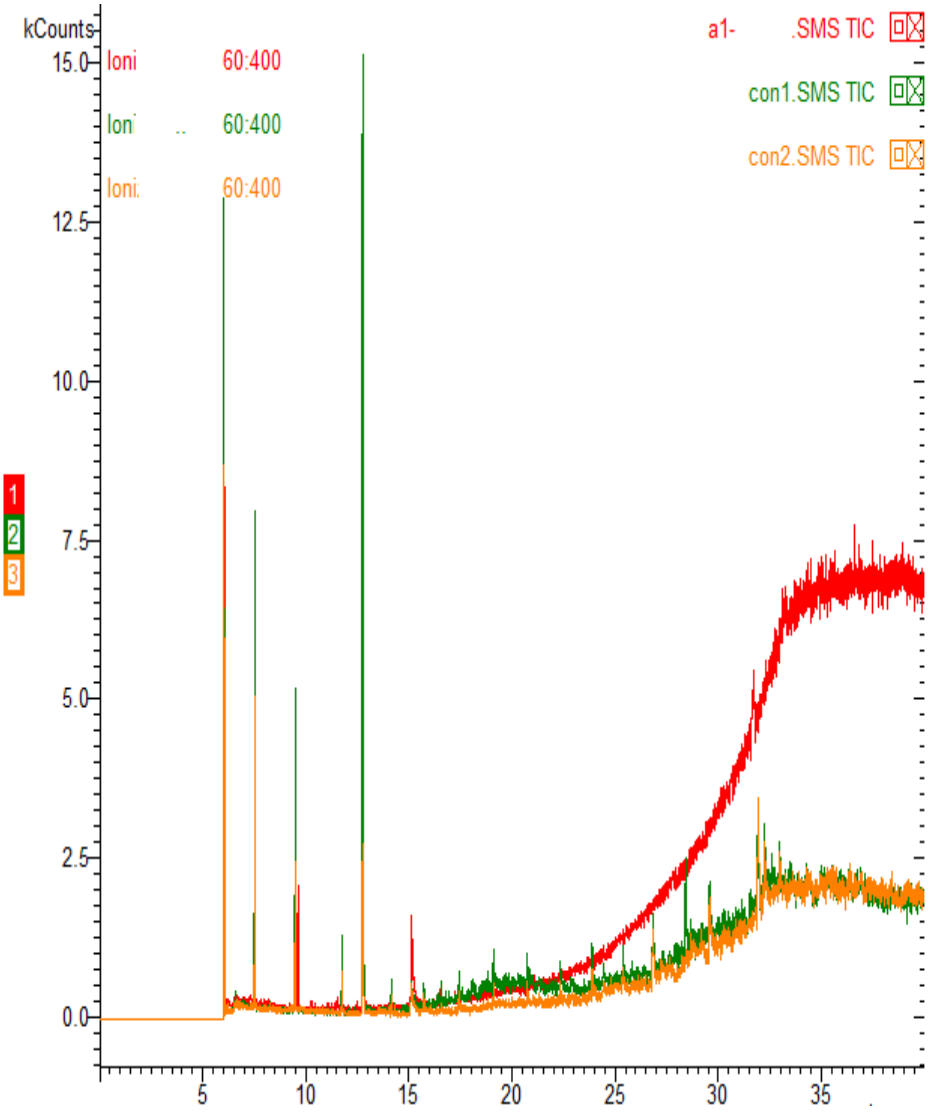


Fig. 27 Cotton a-1 from Egypt and samples con-1,con-2 from Senegal

On axis x time

On axis y intensity signal (k count)

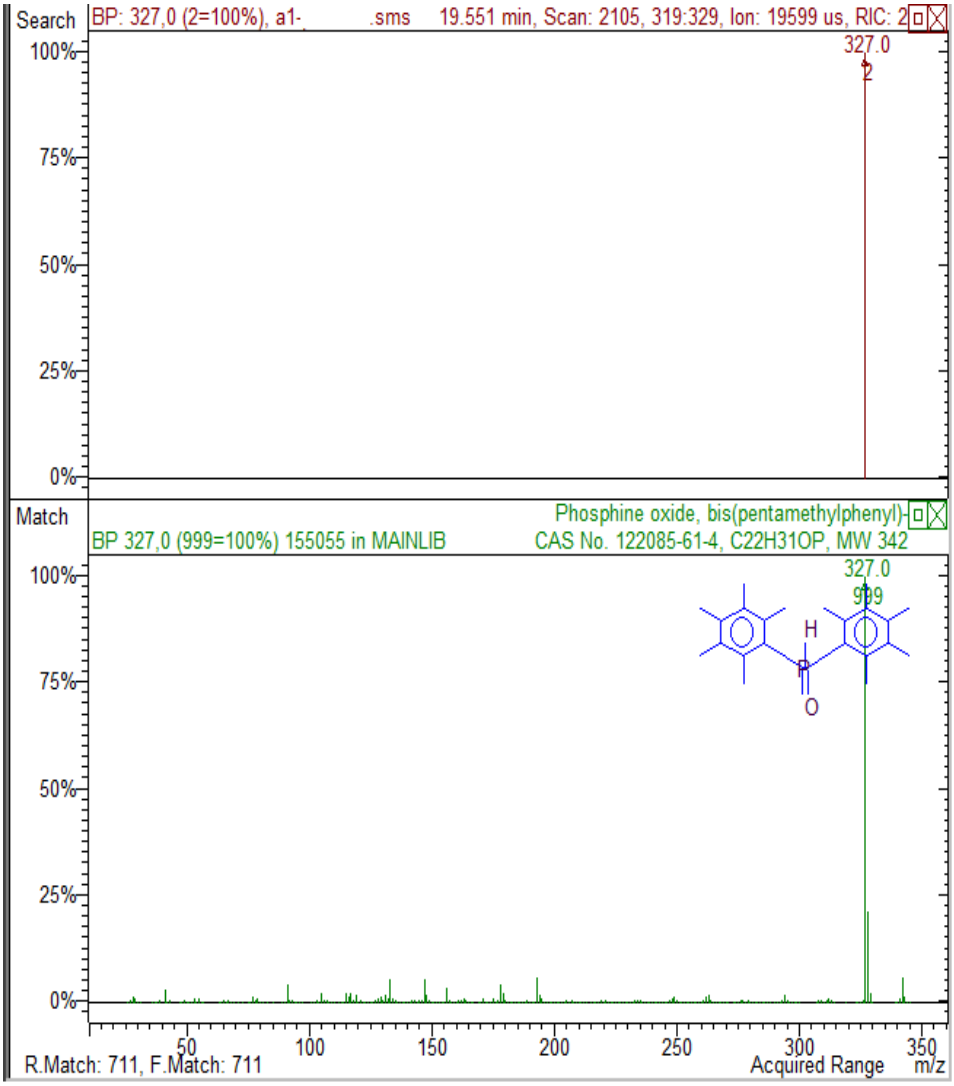


Fig. 28 Evaluation of sample of cotton from Egypt a-1 and Phosphine oxide bis (pentane) from library

RM 711, FM, 711, prob 78.78%, 342 mw formula C22H31OP

In sample c-1from China and sample a-1 from Egypt the same pesticide has been detected

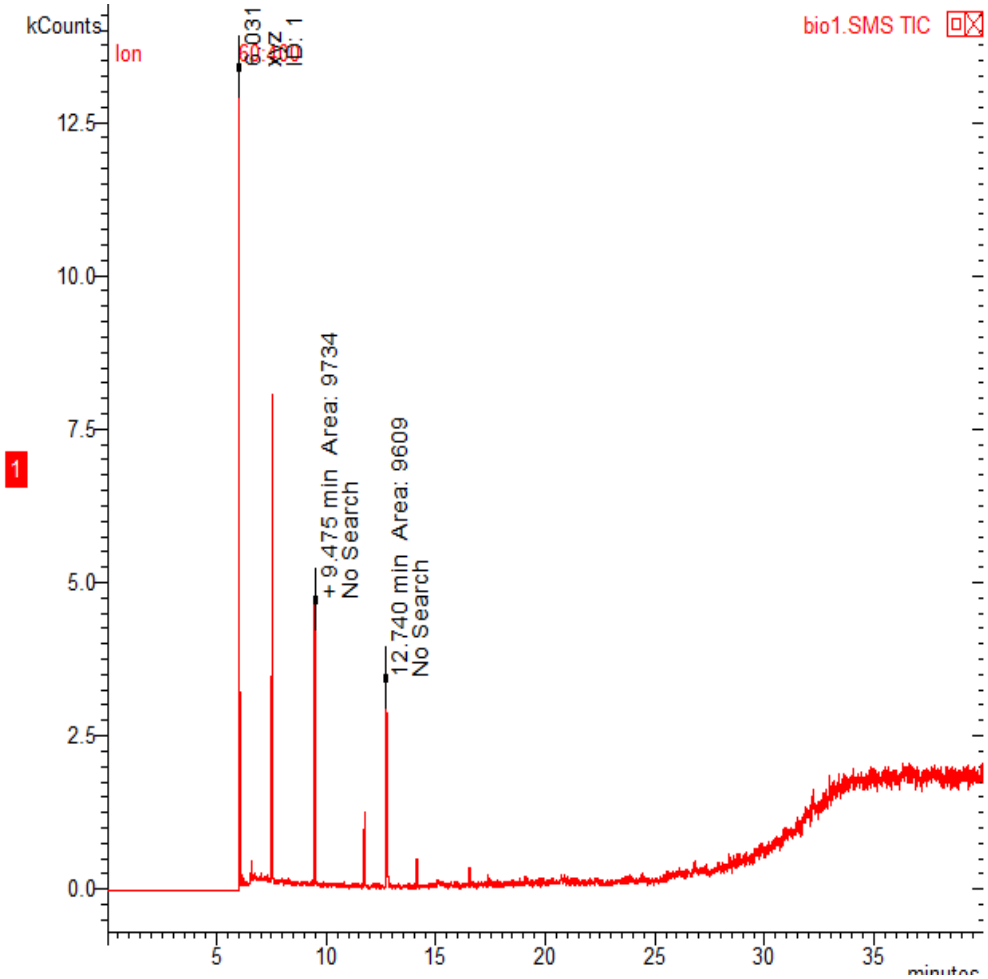


Fig.29 Retention time and peak area of organic cotton bio-1

On axis x time

On axis y intensity signal (k count)

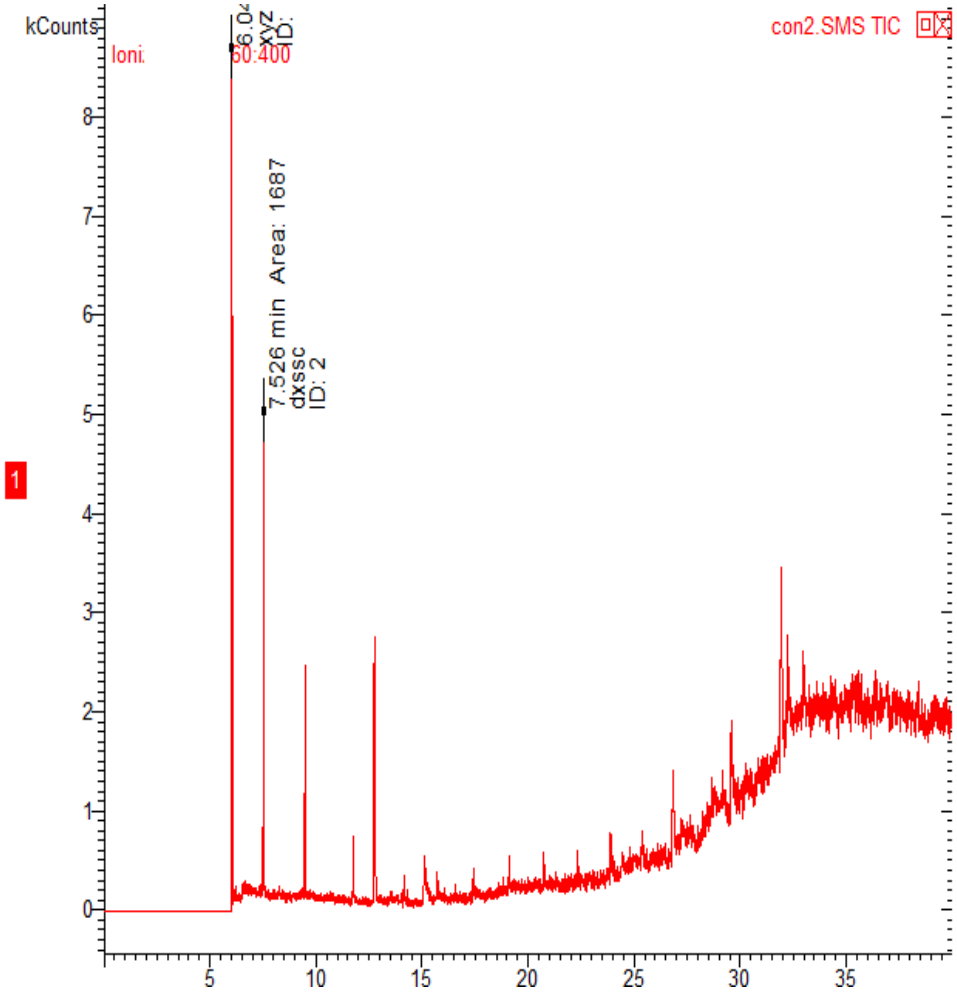


Fig. 30 The retention time and area of conventional cotton

On axis x time

On axis y intensity signal (k count)

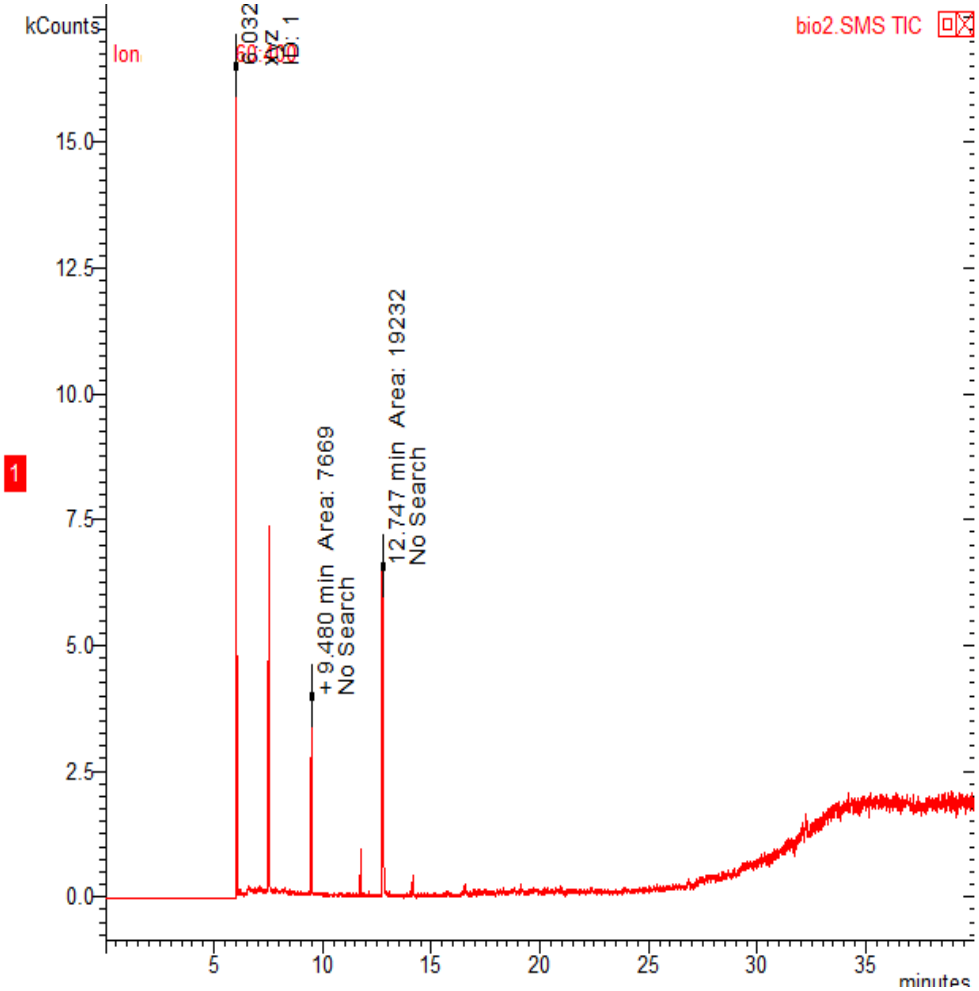


Fig. 31 Retention time and area of conventional cotton con-1

On axis x time

On axis y intensity signal (k count)

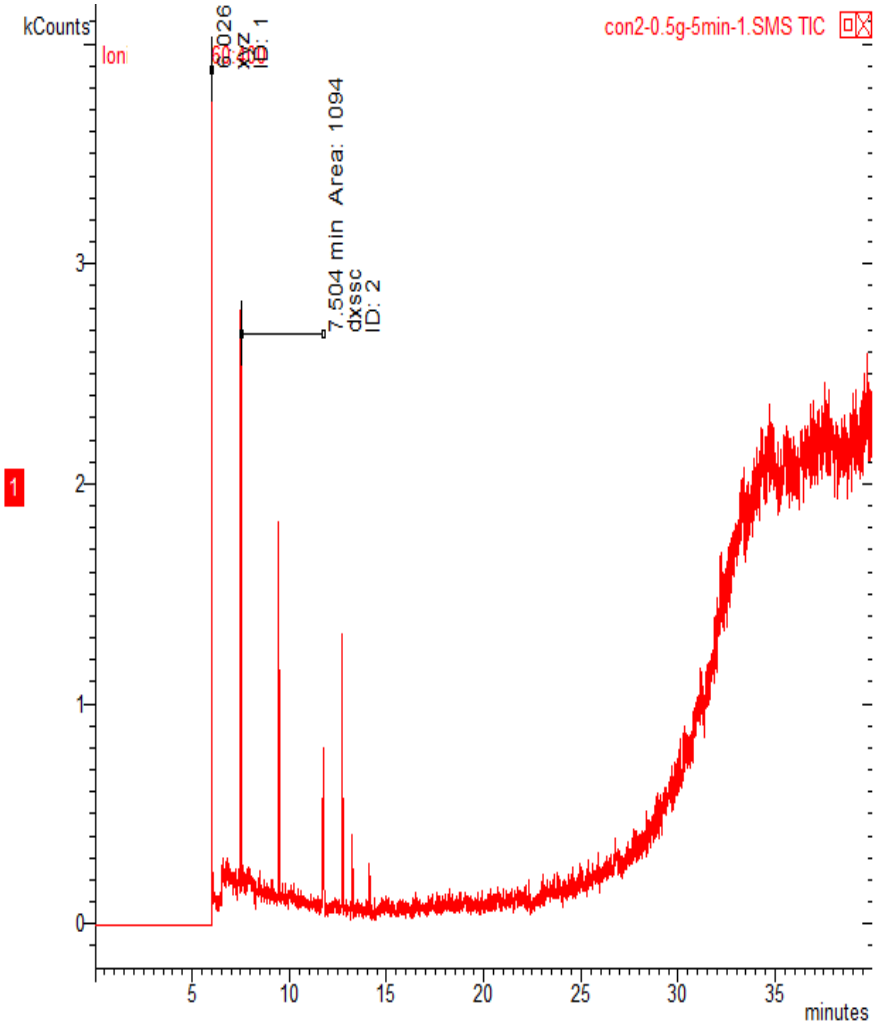


Fig. 32 Retention time and area of conventional cotton con-2 0,5g during 5min

On axis x time

On axis y intensity signal (k count)

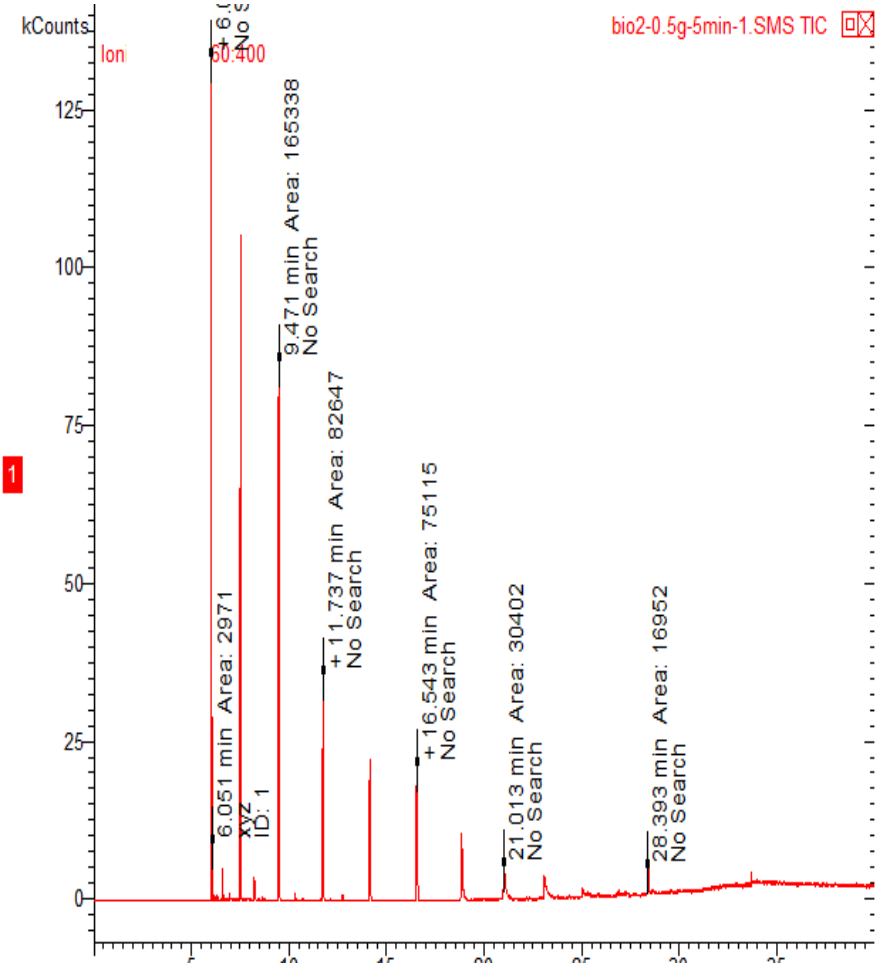


Fig. 33 Retention time and area of organic cotton con-2 0,5g during 5min

On axis x time

On axis y intensity signal (k count)

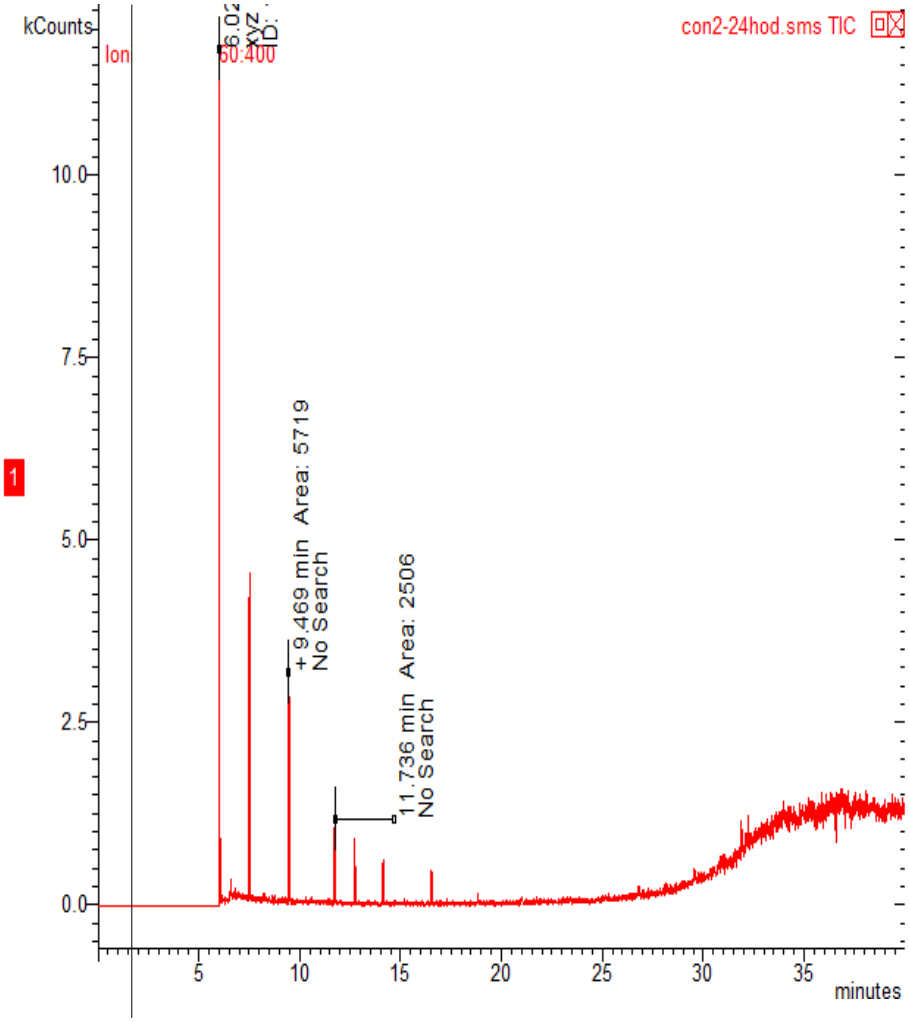


Fig.34 Retention time and area of conventional cotton con-2 0,5g during 24h

On axis x time

On axis y intensity signal (k count)

The aim is to assess different cotton samples according to weight and time in solution. From figures one can learn, name of pesticides, chemical formula, time of retention, area under peak. Such information is needed to conclude that the method is suitable to detect pesticides on cotton fibers.

Tab. 11 Overview of the retention time and peak area

	Bio-2-24h	Bio2 0,5g 24h	Con-1 – 1g 24h	Con-2- 1g 24h	Con-2- 0,5g 24h
time(min)	6,025	6,026	6,035	6,026	6,025
peak area	8739	10246	17491	13395	11216

The results of conventional cotton con-2-24h and organic cotton organic 24h according to the results of the specified retention times to the conventional cotton con2 during 24h larger peak areas are compared. If pesticides are not present in the selected range (Mix-10), it is not possible to detect the presence of pesticides. So, the presence of pesticides, which were of the type used in Senegal, Egypt (sample a-1), Russia (sample b-1), China (c-1) was detected. This is possible to detect, and thus it is recommended to use this method for certifying organic cotton. Conventional and organic cotton have almost the same retention time. Retention time is not sufficient to assess this process.

4.3.2 Measurement of extract of organic and conventional cotton using electrochemical biosensors with acetyl cholinesterase

Principle of measurement

The output signal of the biosensor is measured as current used for relative inhibition

$$RI = \frac{dI}{dt} \times \frac{1}{I} \qquad [s^{-1}] \qquad (26)$$

Relative inhibition is defined by the equation above.

Where steady current I value after the addition of substrate, and dI/dt is the rate of current decrease observed after the addition of the sample with a pesticide. RI value is proportional to the inhibitory effect of organophosphates or carbonates. The value of RI is also proportional to the concentration, but the constant of proportionality is different for each pesticide.

Experimental part:

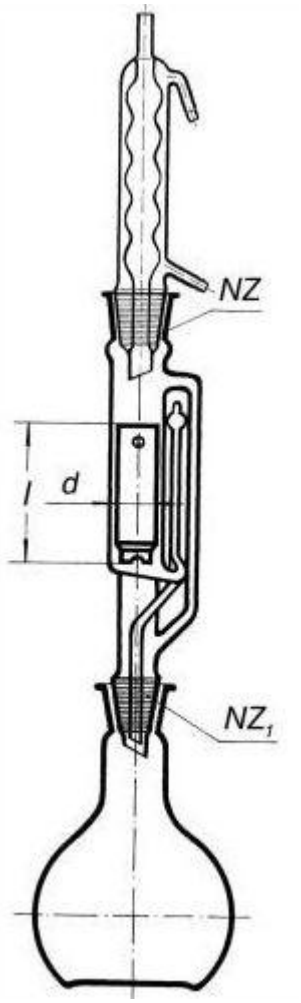


Fig. 35 Soxhlet extraction column

Preparation of extract

Extraction solution: 200 ml = 180 ml 0.04 M MOPS buffer (pH 7.00) + 20 ml CH_3CN

Sample cotton: 2 g

Extraction time: 1 hour Soxhlet column

MFS-USB micro potentiostat system + software

Microfluidic capillary arrangement allows precise and constant flow of solution around the electrochemical active surface of the sensor. This means that the system provides high level of reproducibility and sensitivity. The device has a built in closet where the sensor can be easily

inserted. Furthermore, the system is equipped with a special two-channel pump. The first channel provides mixing of the solution and a second flow of fluid past the sensor is analyzed.

Fig. 36 Micro system potentiostat

At the time of 100s, addition of 20 ml 253 mm ATCH (acetylthiocholine chloride) substrate for the enzyme is done .Measurements are completed after time 400 s. System was washed with distilled water,10 ml extract of cotton was dosed into the MFS and measurements were started. At the time of 100 s - 20 ml of 253 mm ATCH (acetylthiocholine chloride) - substrate for the enzyme was added. At the time of 300s addition of 10 ml of 1.5 mm Syntostigmin (neostigmine methylsulfate) was done as per standard for inhibition of AChE enzyme. Measurements was completed at time 400 min.

Results and discussion

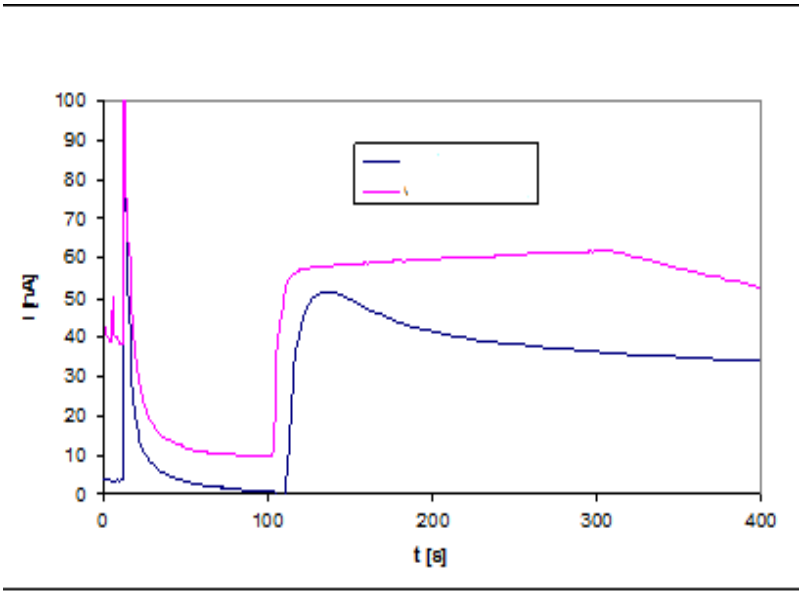


Fig. 37 First measurement with organic cotton bio-2

-blue curve: extract of organic cotton

-red curve: buffer

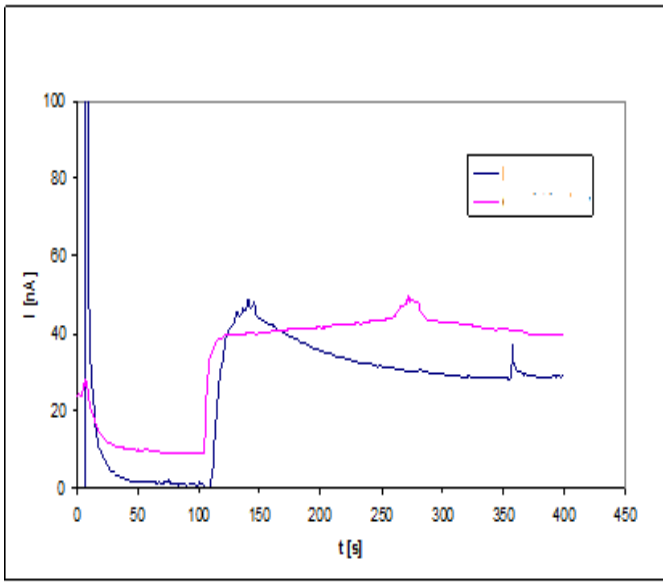


Fig.**38** Second measurement with organic cotton bio-2

-blue curve: extract of organic cotton

-red curve: buffer

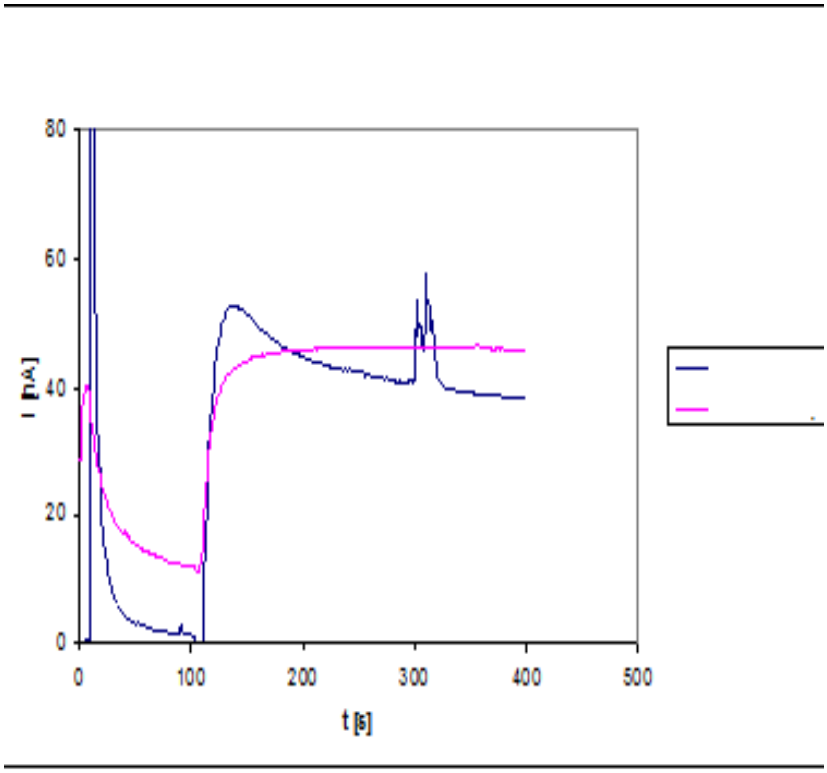


Fig. 39 First measurement with conventional cotton con-1

-blue curve: extract of organic cotton

-red curve: buffer

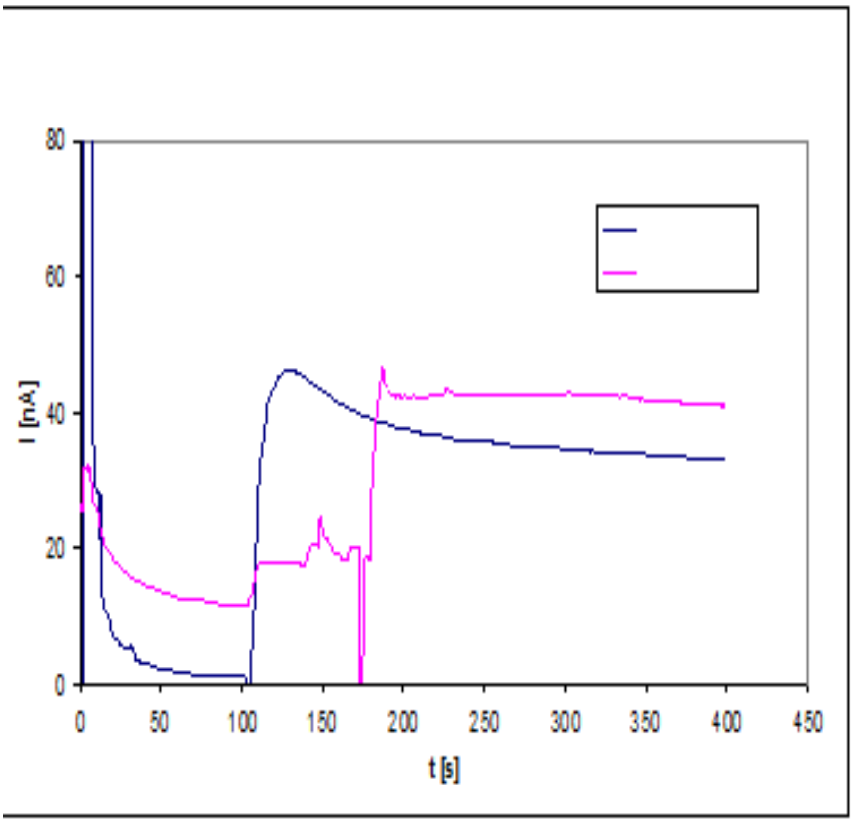


Fig. 40 Second measurement with conventional cotton con-1

-blue curve: extract of organic cotton

-red curve: buffer

Tab. 12 Relative inhibition caused by the inhibitor model Syntostogminem

Type of cotton	Measurement 1 RI [s^{-1}]	Measurement 2 RI [s^{-1}]	average RI [s^{-1}]
Organic cotton bio-2	$1.8*10^{-3}$	$1.2*10^{-3}$	$(1.5 \pm 0{,}3)*10^{-3}$
Conventional cotton con-1	$5.8*10^{-4}$	$7.3*10^{-4}$	$(6.55 \pm 0{,}75)*10^{-4}$

Relative inhibition corresponding to addition of Syntostigminu is higher in extracts of cotton and similar in both conventional and organic cotton. The difference between the extracts of organic cotton and conventional cotton is parameter relative. The values of relative inhibition showed similar results for individual samples of cotton. This led to the principle of

"fingerprint" i.e. typical for a certain type of cotton. This principle is used to determine the biological activity. After starting the measurement, the sensor is first stabilized and the graph is indicated by the arrow in the settling time of 0-100 second. In time of 100 seconds reaction substrate (acetylthiocholine chloride) is added to the enzyme which binds to the active site and creates a product which is electro active. The decomposition causes surge in current. Over time, upon addition of substrate, the signal becomes stable. At the time 300 seconds, a standard Syntostigminu inhibitor is added for the enzyme reaction. The inhibitor blocks the active sites of the enzyme and enzyme-substrate reaction is slower, which is reflected in the graph as decrease in flow measurement time. Optimization of extraction (reduction of extraction, a higher proportion of organic solvent for pre concentration step) method has the potential to distinguish between different types of cotton on the principle of "finger print of organic fibers of plant origin. [23]

4.4 Optical measurement of organic and conventional cotton

SEM for investigating surface properties of cotton is very useful for properties assessment.

4.4.1 Optical measurement of organic and conventional cotton by SEM

Fig. 41 Organic cotton

bi **Fig.** 41 Organic cotton bio-2 from miscrocope SEM

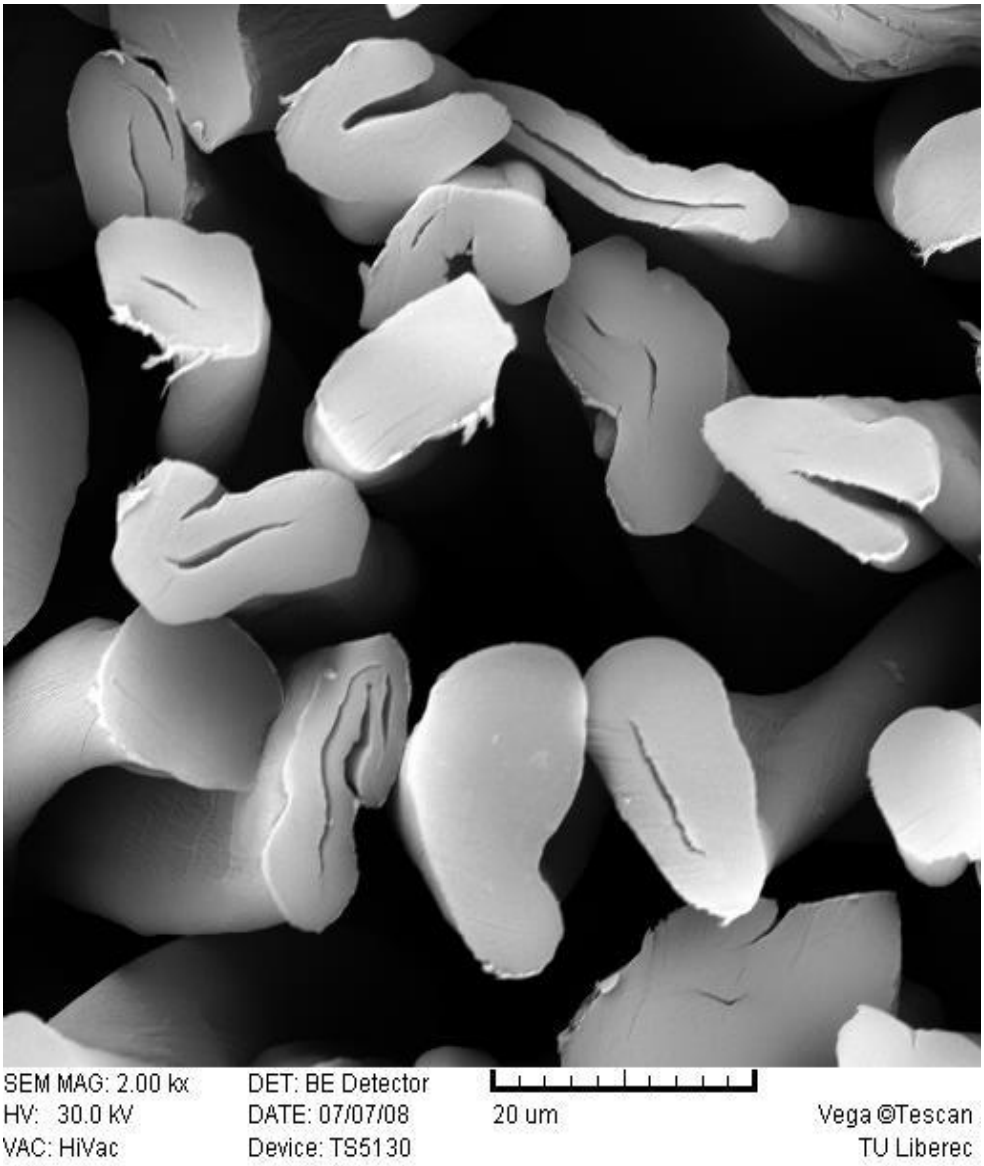


Fig.42 Organic cotton bio-2from miscrocope SEM

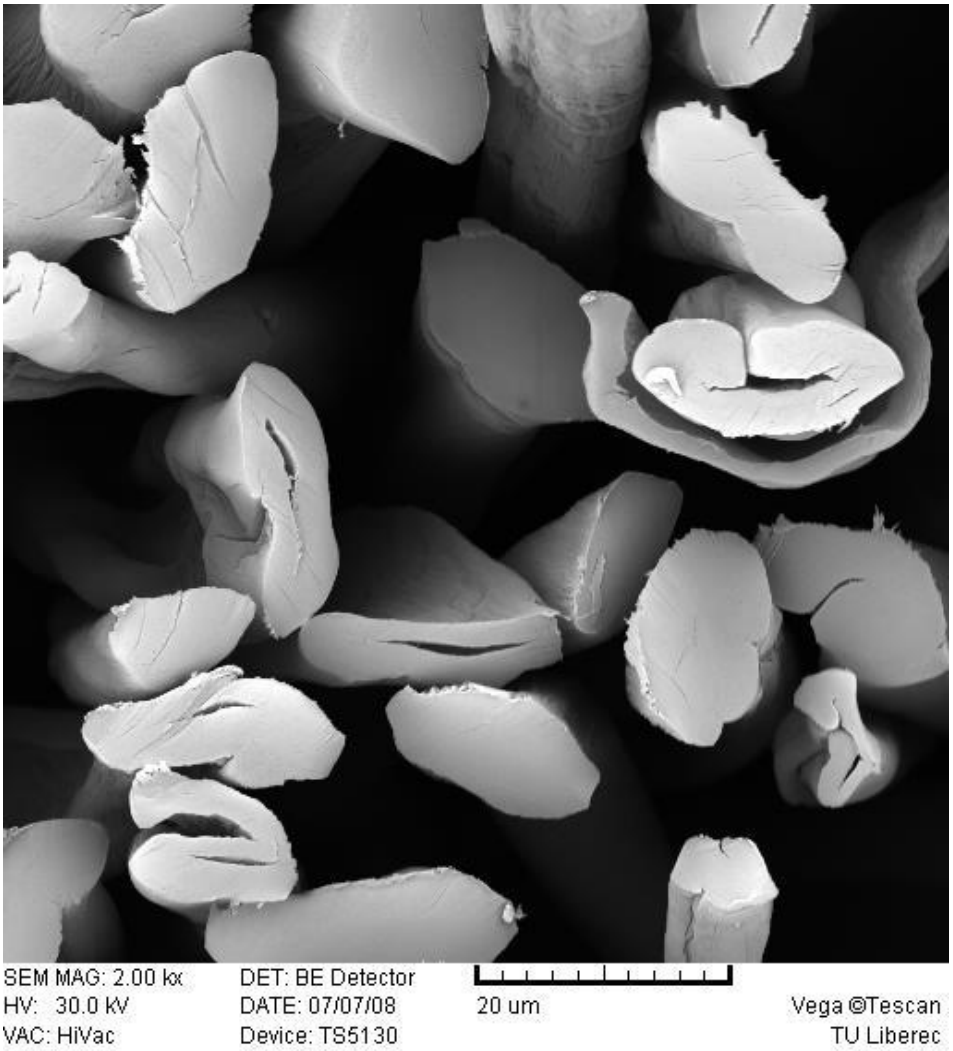


Fig. 43 Conventional cotton con-1from miscrocope SEM

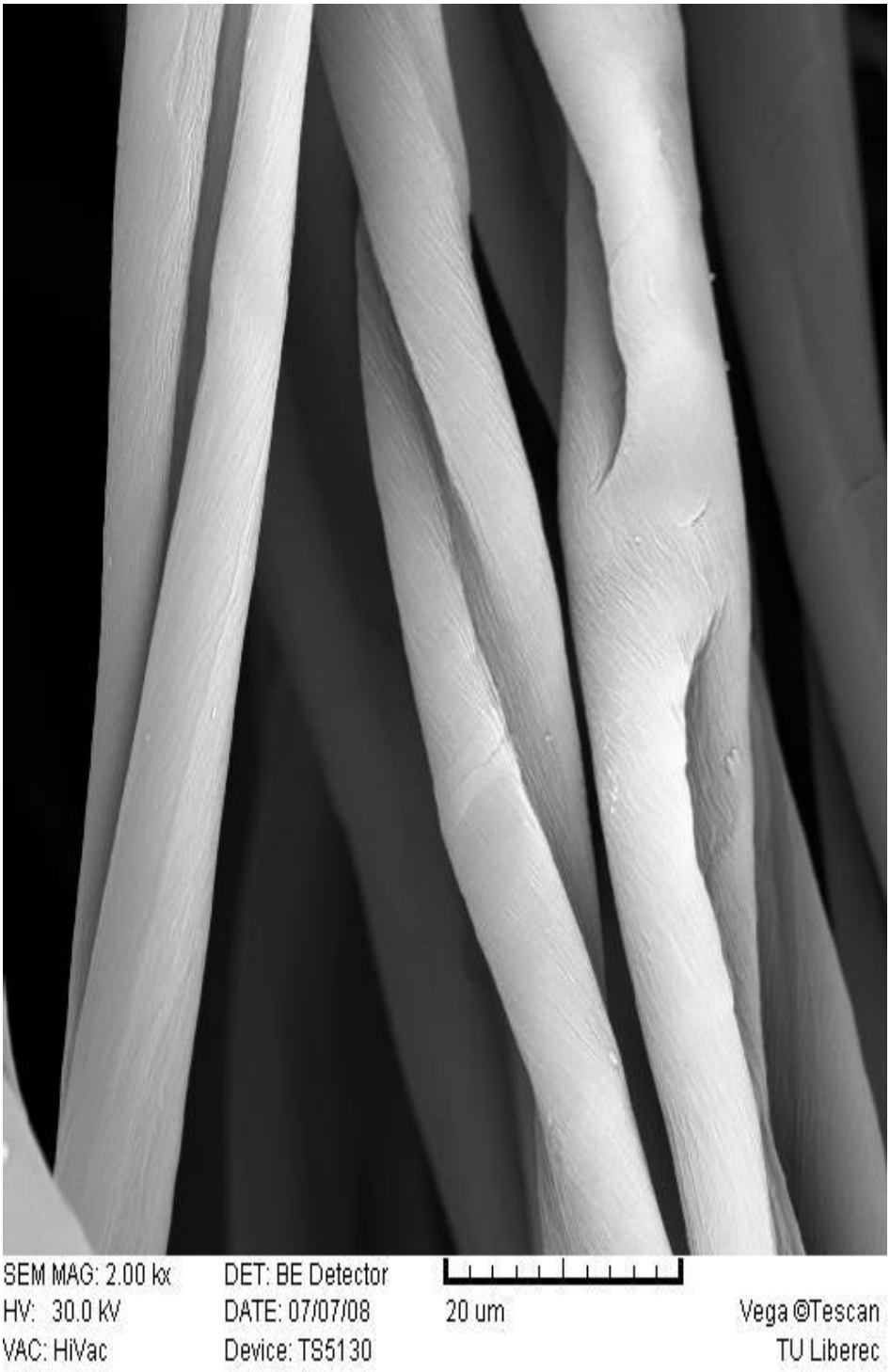


Fig 44 Conventional cotton con-1from miscrocope SEM

4.5 Thermal properties of organic and conventional cotton

Using DSC and TG the thermal properties was investigated

4.5.1 Differential scanning calorimetric DSC

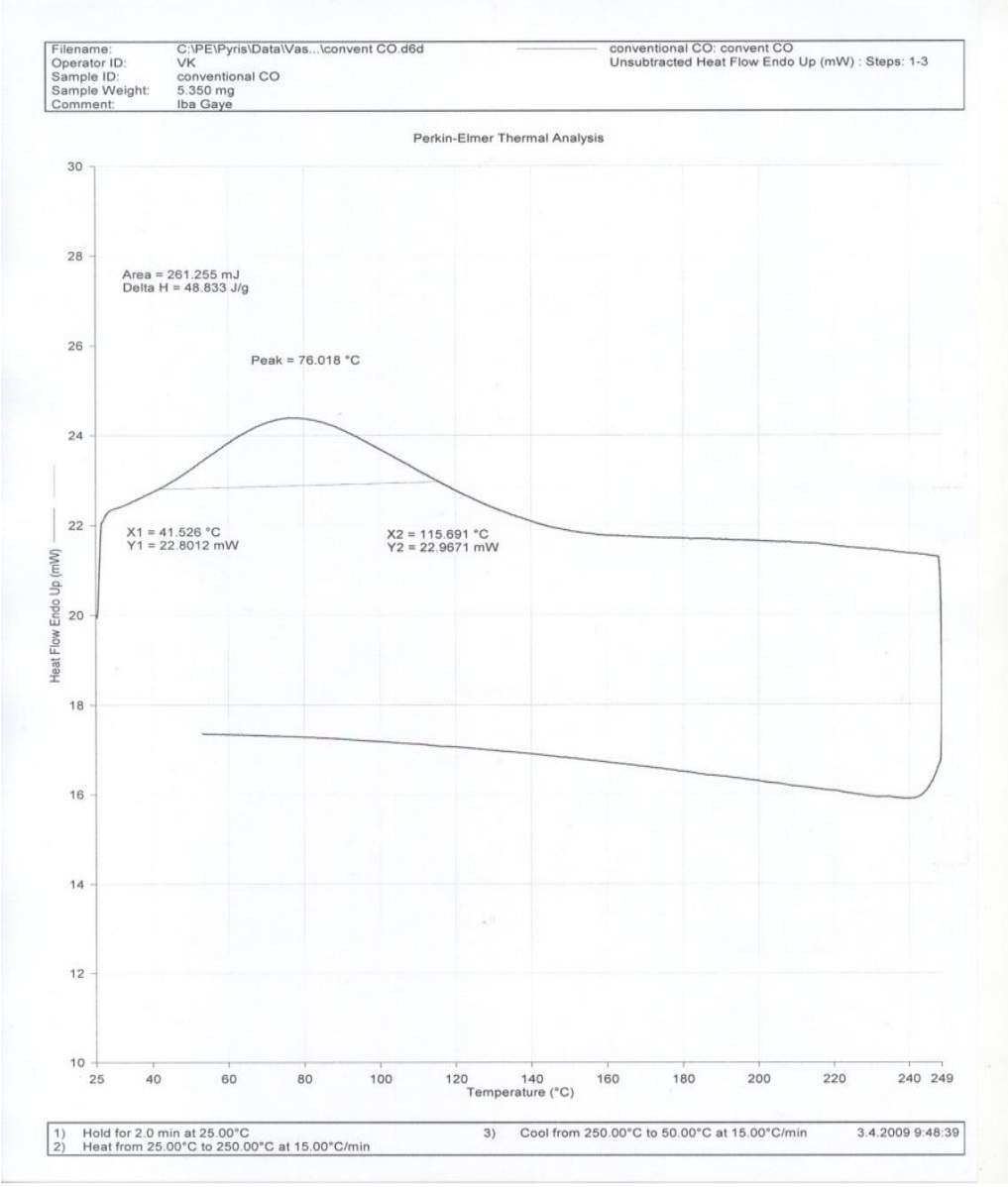


Fig. 45 Graph for conventional cotton con-1 (DSC KTM TUL)

The temperature where water leaving sample of cotton con-1 76,018 ° C for sample weight 5.35 mg Area 261.25 mJ ΔH 48,833 J / g

Destruction and degradation of fiber 220 ° C

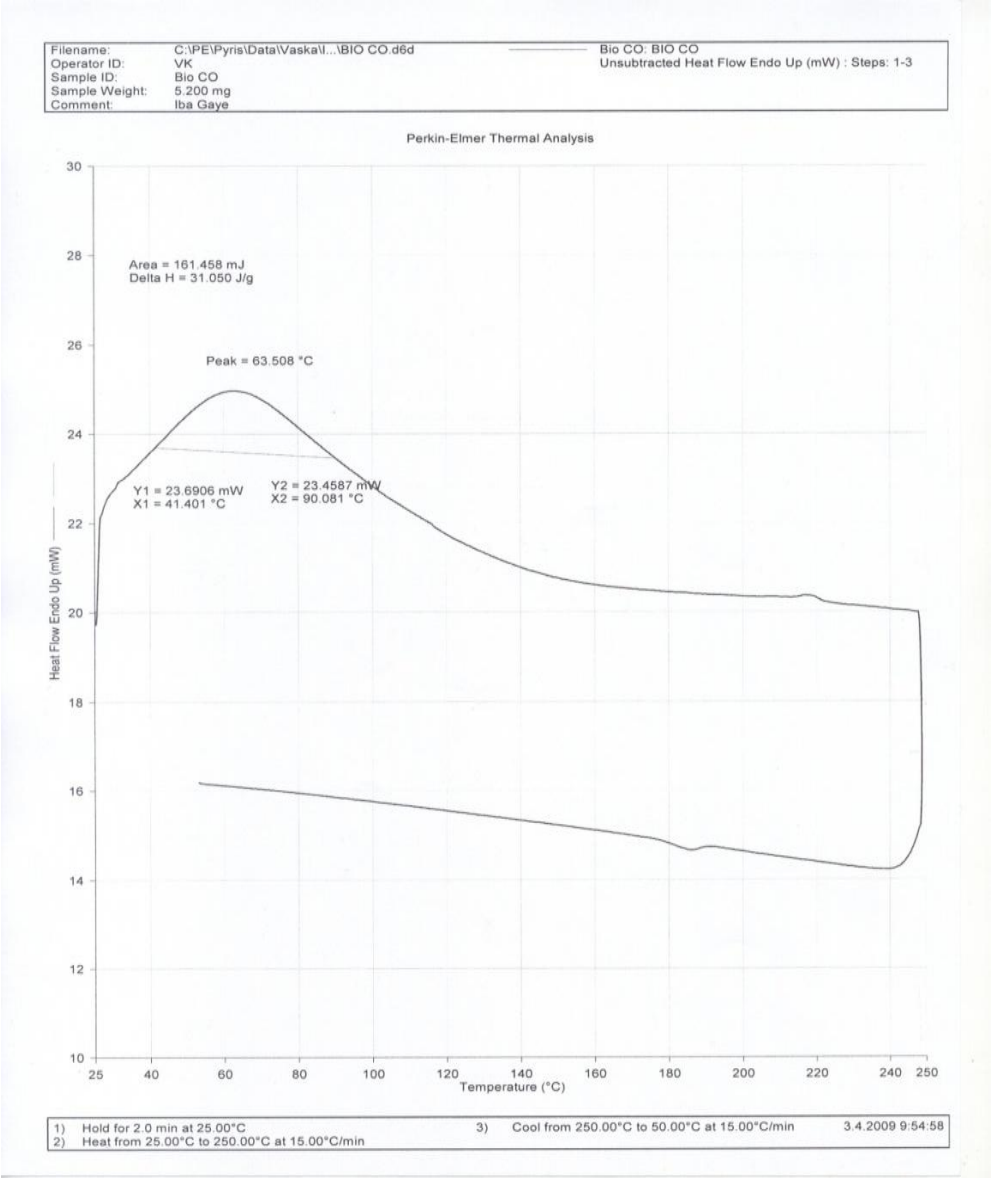


Fig.46 organic cotton bio-2 NA DSC KTM TUL

The graph is subtracted:

Water going out of fiber at temperature 63,508 ° C sample mass 5.200 mg ΔH 31.05 J / g Area 161,458 mJ

Destruction and degradation of fiber about 220 ° C

4.5.2 Thermogravimetric analysis

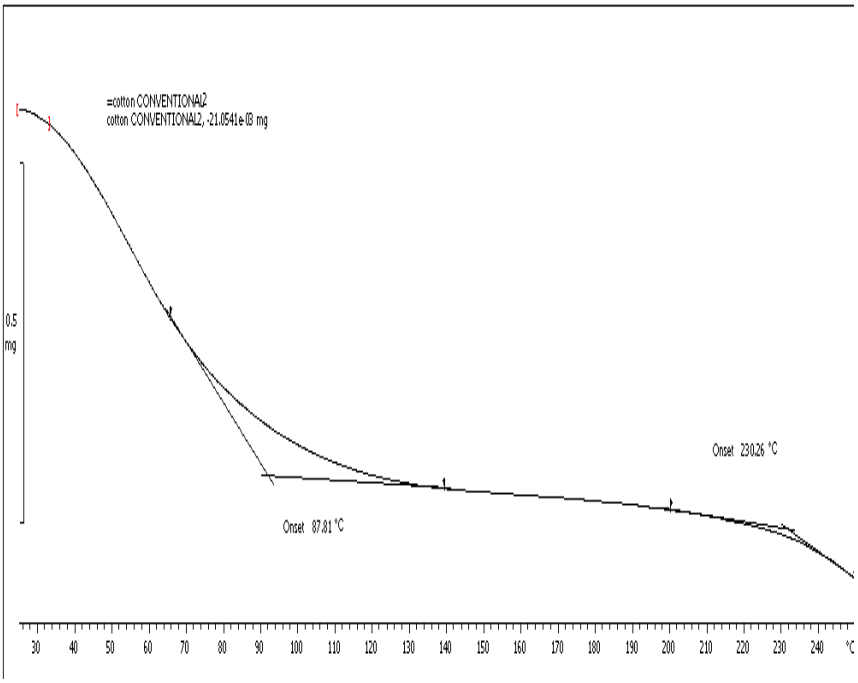


Fig. 47 Thermo gravimetrical analysis (TGA) on conventional cotton con-2

On axis x temperature

On y axis weight

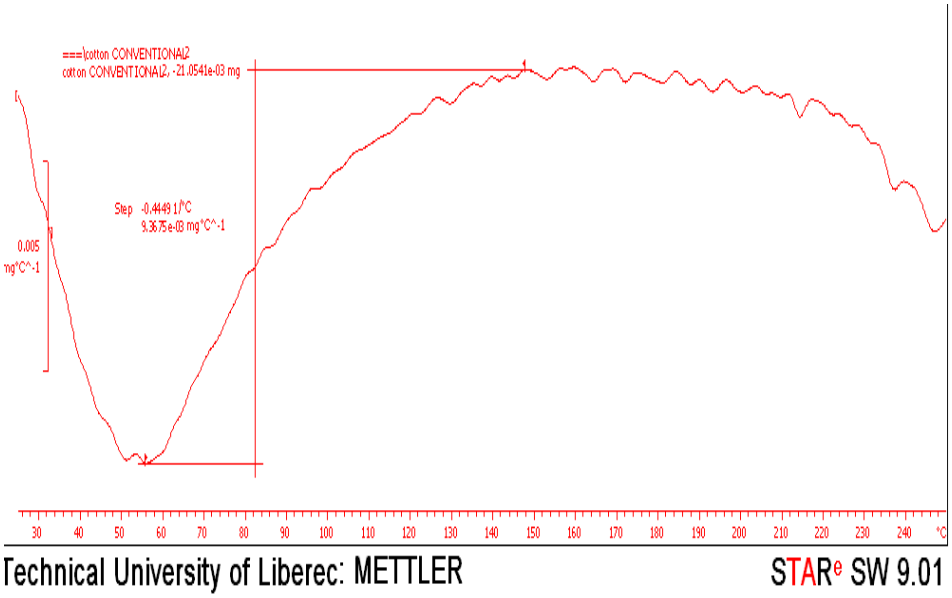


Fig. 48 Thermo gravimetrical analysis (TGA) derivation curve of conventional cotton con-2

On axis x temperature

On axis y weight

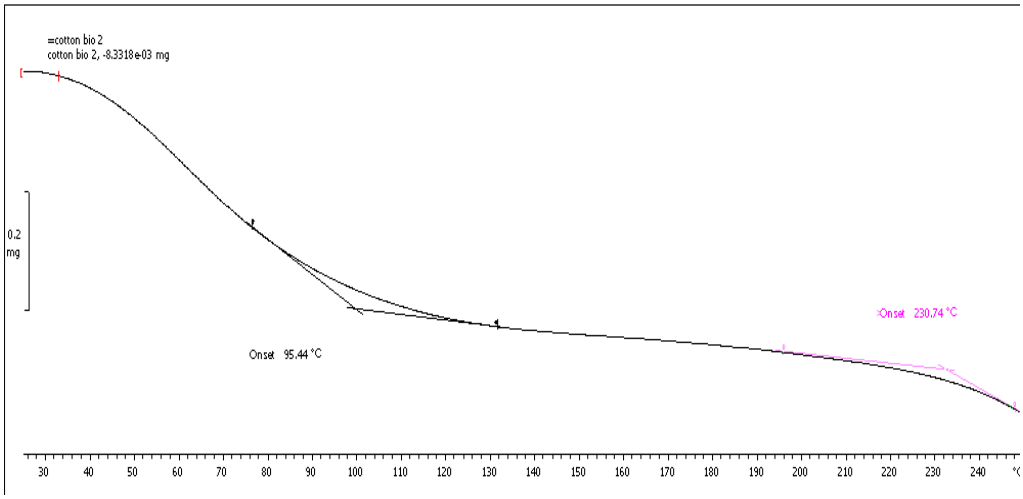


Fig. 49 Thermo gravimetrical analysis (TGA) on organic cotton bio-2

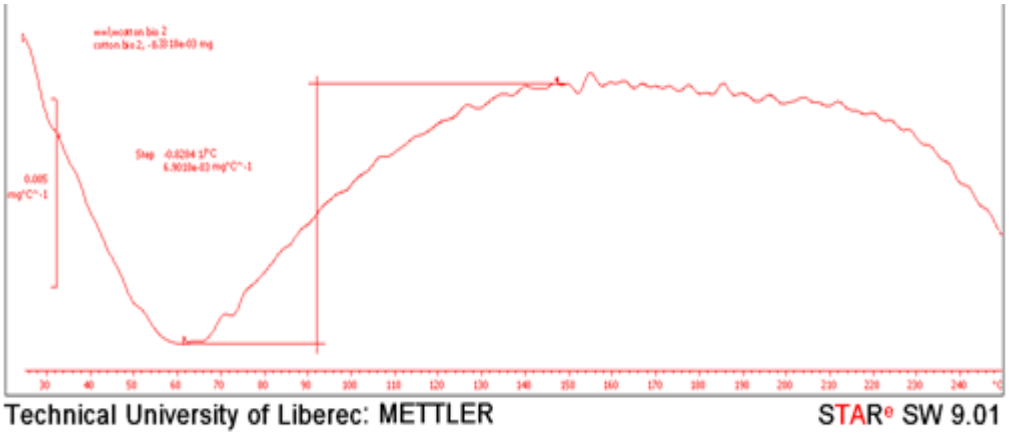


Fig. 50 Thermo gravimetrical analysis (TGA) derivation curve of organic cotton bio-2

On axis x temperature

On axis y weight

5. Results obtained

	T g/g	L mm	M dtex	F dtex	S N/tex	E %	D %	U %
Conventional Cotton con-1	0.01	33	2,35	1,88	7,72	5,81	20	79.3
Organic cotton bio-2	0.01	32	2.23	1,73	7,44	5,13	24	75,41

Tab.13 Summary comparison of results for organic and conventional cotton

T (trash), M (Maturity), F (fineness), S (strength) E (elongation), D (dispersion), L (length), U (uniformity)

Major properties of organic cotton which lead to develop a method which can detect pesticide and very important information about organic cotton were investigated. Such majors characteristics based on available devices, show no big difference between conventional and organic cotton, as can be seen in table (Tab. 13). This methodology can detect pesticides on cotton fiber, giving the chemical formula and the name of the pesticide that is new in this field according to information received from the general manager of the international organization working with cotton named ICAC (International Organization for consultations with cotton).

5. Evaluation of results, the practical lessons learnt and general conclusion for practice

A methodology that allows detection of pesticides in cotton sample from Senegal and other countries of Russia, India and Egypt is proposed. The methodology is able to give the name of the chemical pesticides and formula of pesticide. Nowadays the properties of organic and conventional cotton are available. It is very difficult to distinguish biotechnology cotton, conventional cotton and organic cotton. Organic cotton is getting the benefits of the market in terms of trade as a whole, but conventional cotton price is determined by the class, which may affect. The proposed methodology could be applied to others naturals fibers, but of course it is necessary to study all properties of samples deeply in order to assess and finally to decide the suitable fiber.

This methodology can be applied in others fields like toxicology, pharmaceutical or tracking drug on blood Marginal revenue may be interesting for farmers in case of organic cotton. Africa must be more competitive in terms of productivity and quality: compared to its competitors in the world market.

6. Conclusion and discussion

Some argue that simply pesticides do not exist on cotton as confirmed by Institut in Bremen Germany. It is confirmed that it is impossible to detect pesticides on cotton, but the developed methodology detected pesticide in cotton fiber; it gives the chemical of pesticide and the name of the pesticide. Based on their tests on samples of cotton from Senegal, but under the proposed detection methodology that was developed in department of mechatronics, Institute of nanotechnology, and Applied Informatics, the chemical pesticides can be detected. The pesticides tests were conducted also with the old cotton samples (15 years) of cotton (Syria, Egypt, and China). The methodology developed in this thesis, today confirms that this method can detect pesticide for cotton.

Based on this work, one can detect traces of pesticides in conventional and organic cotton through the proposed method using the apparatus GC-MS gas chromatography with mass spectrum variant 3800/2000, based on the principle that is proposed in this work. It confirmed the presence of pesticides that were used in Senegal (con-1, con-2), in Egypt (sample A-1), in Russia (comp b-1), in China (comp c-1). That is why it is recommended for the certification of organic cotton and all natural fibers from plants, Variant 3800/2000 gives better resolution of the presence of pesticides in cotton fiber. In terms of the properties, the organic and conventional cotton is not very different (see comparison table). This method to detect pesticides in cotton samples, which was an intention , to distinguish between organic cotton and conventional cotton is acceptable. I want notified that the DMA and DSC shows some different measurement for organic and convention cotton. GC gives a same results for retention time of organic and conventional cotton and may be not influenced by weight or eluted time(Tab.11) The problem is the fact that the organic cotton needs a lot of Nitrogen and flowering plant must be able to get it out of the soil by use of organic fertilizer for the rapid development of cotton; the use of biotechnological cotton is needed in this case to establish a clear legislation. This is due to the fact that chemicals from conventional cotton stretch, but samples from Egypt and China, also demonstrated pesticides. Importance of promoting organic plants underlines issues and characteristics of organic cotton and conventional cotton and how to determine pesticides in cotton fiber and thus certified as organic cotton and naturals plants. The mechanical properties with Vibroscope and the thermal properties with DSC Shows also some difference between organic and conventional cotton May be devices as

spectrometer with higher frequency type MS / (magnetic resonance spectrophotometer with a frequency of 1 GHz , spectrophotometer type 66 FT-IR or PACVD device would certainly achieve better distinctiveness, but this method using GC/MS Varian 3800/2000 guarantees to detect pesticides in cotton fibers and a way to determine the certification of organic natural fibers. The methods of detection of pesticides by GC-MS 3800/2000 which is proposed in this work will help for better understanding how to certify organic fiber plant origin by GC-MS Varian 3800/2000. Results from differential scanning calorimetry DSC show the difference between conventional and organic cotton from Senegal in enthalpy and temperature of the water leaving the sample according to TG.

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